New activity coefficient model for correlation and prediction of phase equilibria

Yoshio Iwai

Department of Chemical Engineering, Kyushu University,
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

e-mail address : iwai@chem-eng.kyushu-u.ac.jp

Outline

Background

Calculation of phase equilibria by activity coefficients

Problems of widely used models for activity coefficients

Calculation of interaction numbers

Lennard-Jones fluids by molecular dynamics simulation

New model of activity coefficients

Y. Iwai, Fluid Phase Equilibria 465 (2018) 24-33

Y. Iwai, R. Seki, Y. Tanaka, Fluid Phase Equilibria 488 (2019) 62-71

Applications of new model

Convex behavior in the dilute region

Exceptionally high values in the dilute region

VLE+LLE for binary and ternary systems

Extend to group contribution method

Conclusion

Calculation of phase equilibria

In the field of chemical engineering, the knowledge of phase equilibria is useful for process design.

Calculation methods for phase equilibria

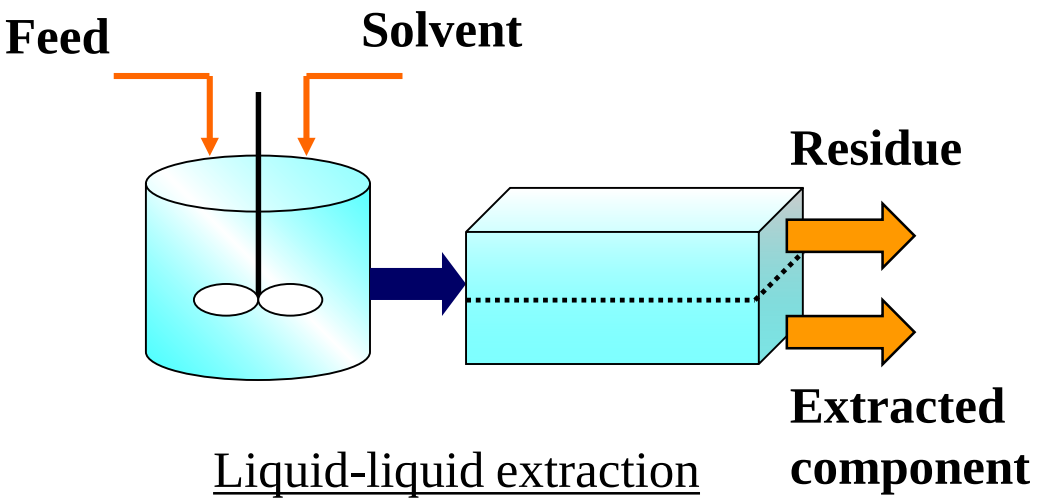
Activity coefficient （Low pressure）

Equation of state （High pressure）

- Vapor-liquid equilibria
- Liquid-liquid equilibria

$$py_i = \gamma_i x_i p_i^{\circ}$$

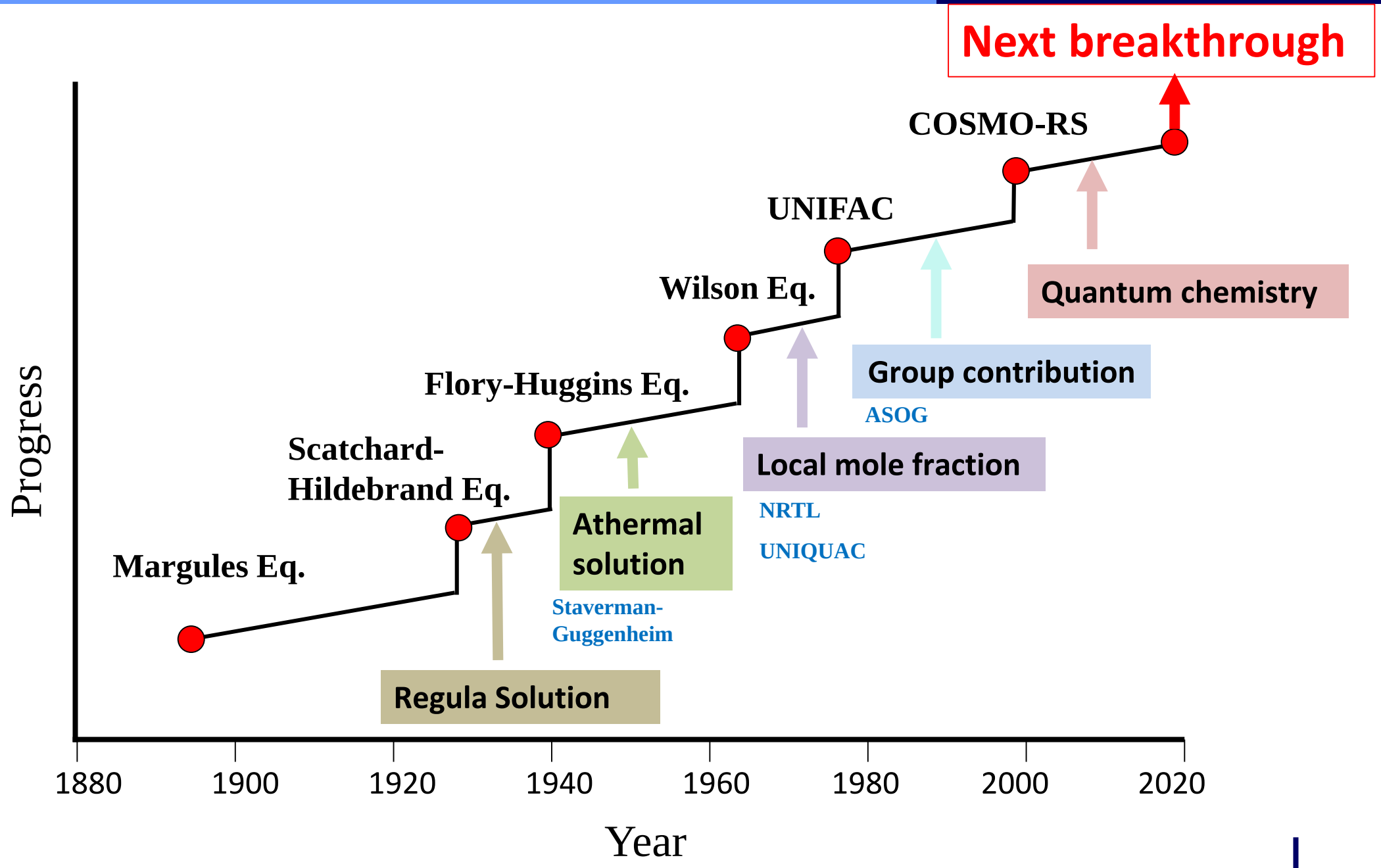
$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}}$$



Liquid-liquid extraction

p; Total pressure, p°; Saturated vapor pressure
γ; Activity coefficient, x, y; mole fraction

Progress of activity coefficient models

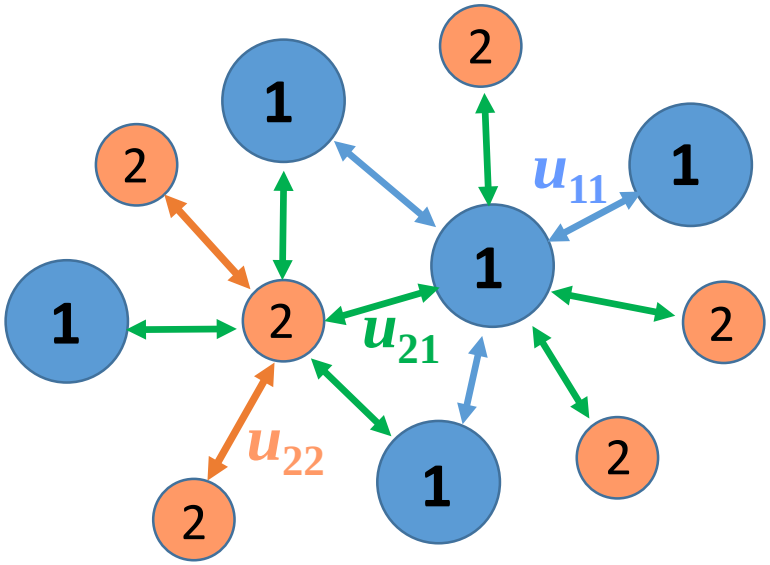


Correlation and Prediction methods

	Correlation	Prediction
Concept	Parameters in models are optimized by experimental data.	Calculations can be done without experimental data.
Advantage	Accurate calculation can be expected for specific systems.	Experimental data are not required. Search for solvents.
Disadvantage	Experimental data are required.	Accurate calculation cannot be expected for specific systems.
Example	Wilson, NRTL, UNIQUAC	UNIFAC, ASOG, COSMO-RS

Both methods are required for process design.

Correlation method



- Intermolecular potentials are the most important parameters.
- The intermolecular potentials are determined to reproduce the experimental data of activity coefficients.
- NRTL [1)] and UNIQUAC [2)] are widely used for correlation models

[1] H. Renon, J. M. Prausnitz, AIChE J., 14 (1968) 135-144.

[2] D. S. Abrams, J. M. Prausnitz, AIChE J., 21(1975) 116-128.

NRTL and UNIQUAC models

NRTL[1)]

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

$$\ln G_{12} = -\alpha_{12} \tau_{12}$$

$$\ln G_{21} = -\alpha_{21} \tau_{21}$$

$$\tau_{12} = \frac{\Delta g_{12}}{RT} = \frac{U_{12} - U_{22}}{RT}$$

$$\tau_{21} = \frac{\Delta g_{21}}{RT} = \frac{U_{21} - U_{11}}{RT}$$

UNIQUAC [2)]

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

$$\ln \gamma_i^C = (1 - V_i + \ln V_i) - \frac{z}{2} q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right)$$

$$\ln \gamma_i^R = q_i \left(1 - \ln \frac{\sum_j q_j x_j \tau_{ji}}{\sum_j q_j x_j} - \sum_j \frac{q_j x_j \tau_{ij}}{\sum_k q_k x_k \tau_{kj}} \right)$$

$$V_i = \frac{r_i}{\sum_j x_j r_j}$$

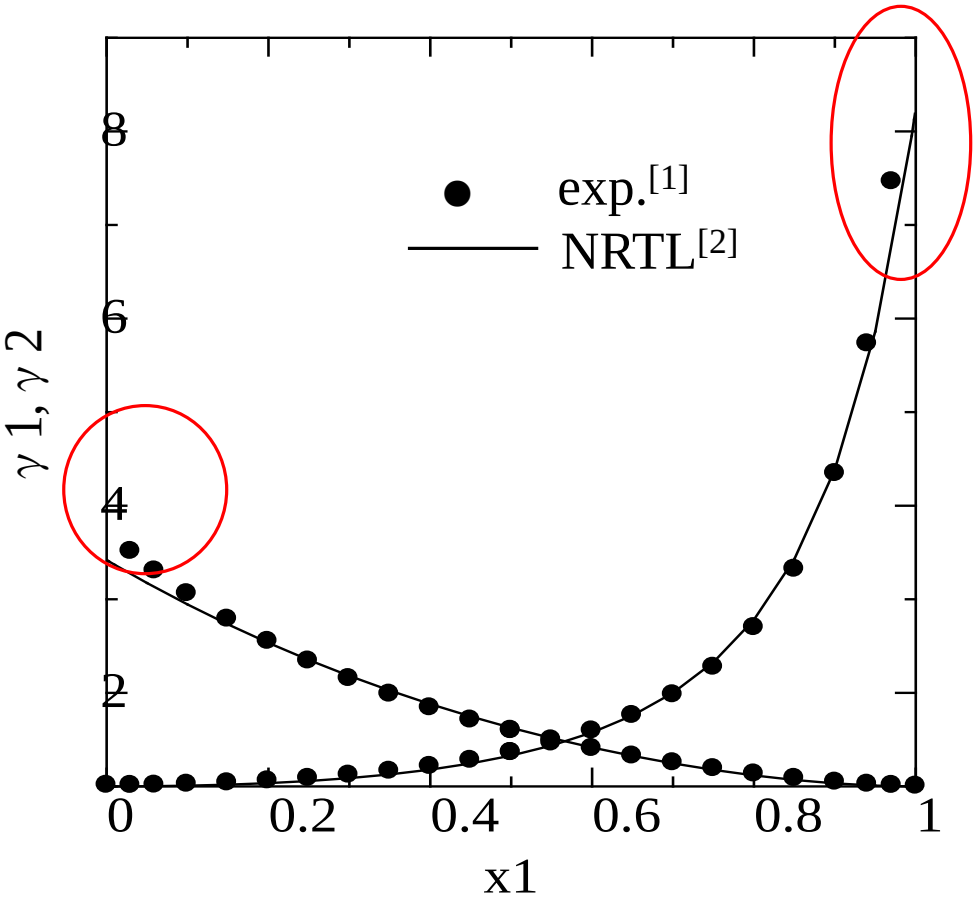
$$F_i = \frac{q_i}{\sum_j x_j q_j}$$

$$\tau_{ij} = e^{-\Delta u_{ij}/RT}$$

$$\Delta u_{ij} = u_{ij} - u_{ii}$$

[1] H. Renon, J. M. Prausnitz, AIChE J., 14 (1968) 135-144.
[2] D. S. Abrams, J. M. Prausnitz, AIChE J., 21(1975) 116-128.

Problems of UNIQUAC and NRTL models (1)



benzene(1)+1-propanol(2) 40℃

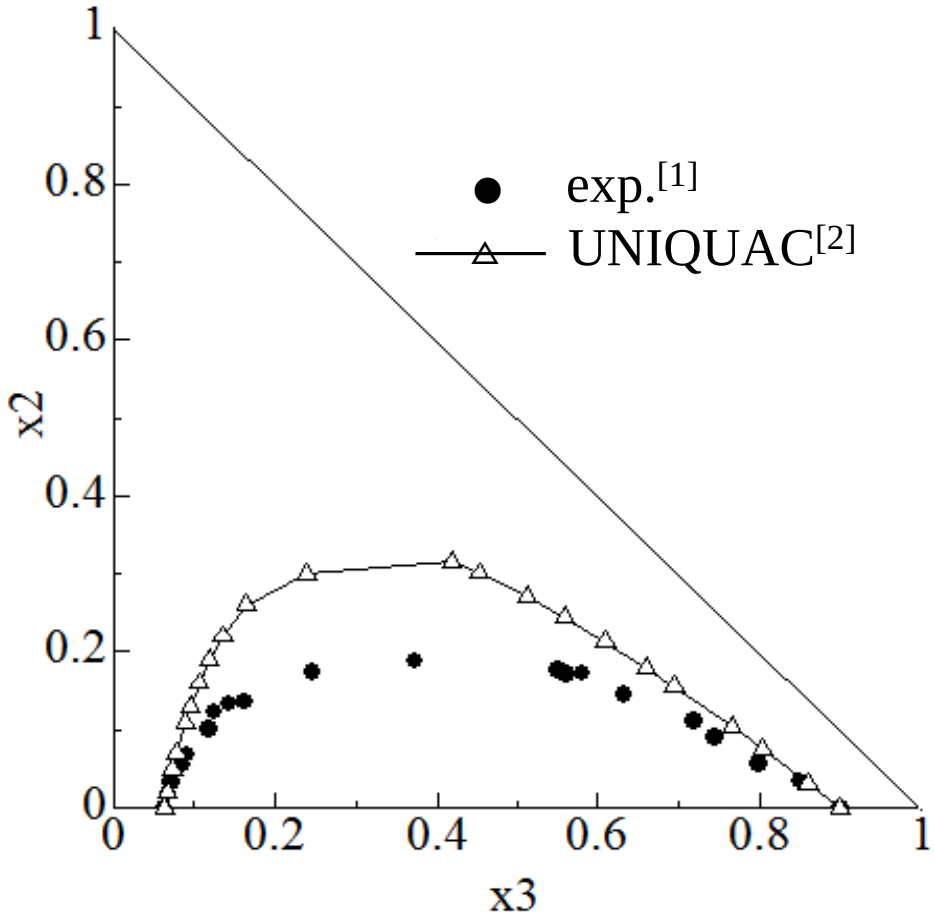
The parameters are fitted to activity coefficients at finite concentrations.

⬇

The estimation accuracy at dilute concentration is no good.

[1] D. A. Palmer, B. D. Smith, J. Chem. Eng. Data, 17 (1972) 71.
[2] H. Renon, J. M. Prausnitz, AIChE J., 14 (1968) 135-144.

Problems of UNIQUAC and NRTL models (2)



acetonitrile (1)+ benzene (2)+heptane (3)
318.15K

The binary parameters are determined by the constituting binary systems.

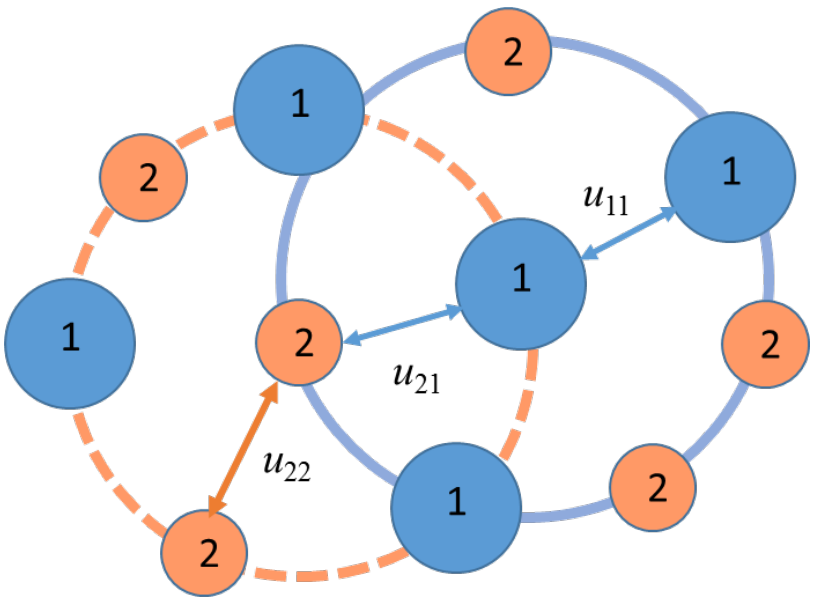
⬇

The deviation of ternary liquid-liquid equilibria is large.

[1] D. A. Palmer, B. D. Smith, J. Chem. Eng. Data, 17 (1972) 71-76.

[2] D. S. Abrams, J. M. Prausnitz, AIChE J., 21(1975) 116-128.

Problems of UNIQUAC and NRTL models (3)



$$\frac{\theta_{21}}{\theta_{11}} = \frac{\theta_2}{\theta_1}\exp\left[\frac{-(u_{21}-u_{11})}{kT}\right]$$

$$\frac{\theta_{12}}{\theta_{22}} = \frac{\theta_1}{\theta_2}\exp\left[\frac{-(u_{12}-u_{22})}{kT}\right]$$

$$N_{21} = 2q_1N_1\theta_{21} \qquad N_{12} = 2q_2N_2\theta_{12}$$

$$N_{21} \neq N_{12}$$

N_i ; Number of molecules i
N_{ij}; Number of interaction pairs ij counted from j
q ; surface area parameter (number of interactions)
u ; interaction energy
θ_j ; surface area fraction of component i
θ_{ij} ; local surface area fraction of component i around component j
i, j; components i, j

Flemr wrote as “The local composition equations are not consistent with the models from which were derived and that they should be treated as only empirical ones.” [1]

[1] V. Flemr, Collection Czechoslo. Chem. Commun., 41, (1976) 3347-3349.

Concept of quasi-chemical model [1]

$$①\underset{u_{11}}{\leftrightarrow}① \;+\; ②\underset{u_{22}}{\leftrightarrow}② \;\rightleftarrows\; 2①\underset{u_{12}}{\leftrightarrow}②$$

$$N_{11} = q_1 N_1 \theta_{11} \qquad N_{22} = q_2 N_2 \theta_{22} \qquad N_{21} = 2q_1 N_1 \theta_{21} = N_{12} = 2q_2 N_2 \theta_{12}$$

$$\frac{N_{12}^2}{N_{11}\,N_{22}} = 4\exp\left[\frac{-\left(2u_{12} - u_{12} - u_{22}\right)}{kT}\right] \qquad \frac{\theta_{11}\theta_{22}}{\theta_{21}\,\theta_{12}} = \exp\left[\frac{2u_{12} - u_{11} - u_{22}}{kT}\right] = \tau_{12}$$

$$\ln \gamma_i = q_i \ln \frac{\theta_{ii}}{\theta_i}$$

τ_{12} and q_i are parameters (constants)

N_i ; Number of molecules i
N_{ij}; Number of interaction pairs ij counted from j
q ; surface area parameter (number of interactions)
θ_j ; surface area fraction of component i
θ_{ij} ; local surface area fraction of component i around component j

γ ; activity coefficient
k ; Boltzmann constant
T ; temperature
u ; interaction energy
subscripts
i, j; components i, j

[1] E. A. Guggenheim, Mixtures, Oxford Univ. Press, London (1952).

Molecular dynamics simulation in liquid phase

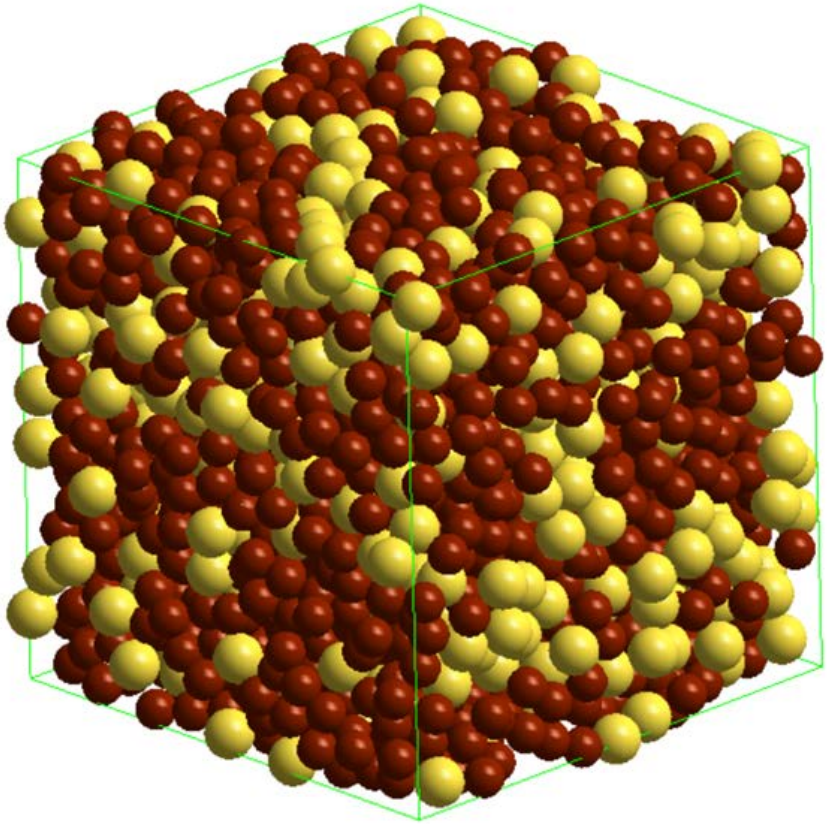
Lennard-Jones(LJ)

$$\Phi_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Lorentz-Berthelot combining rules

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

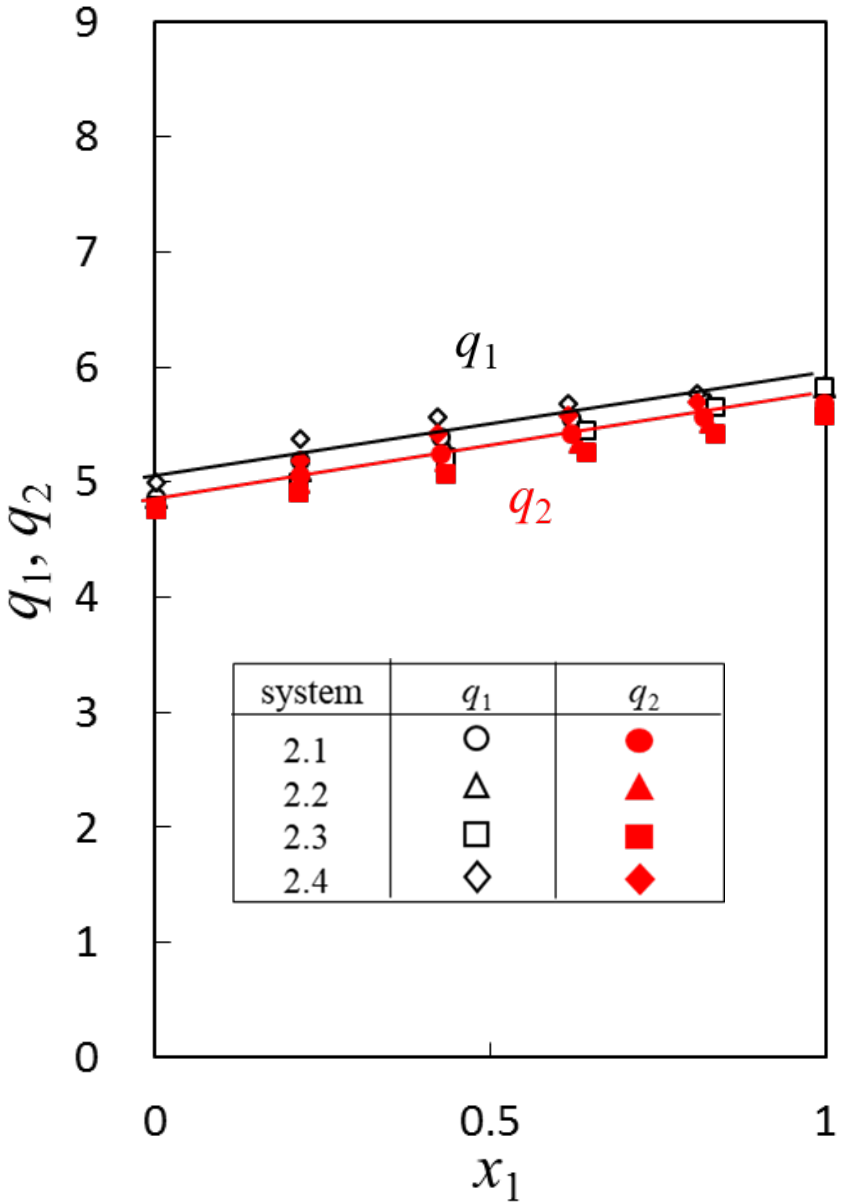
$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$

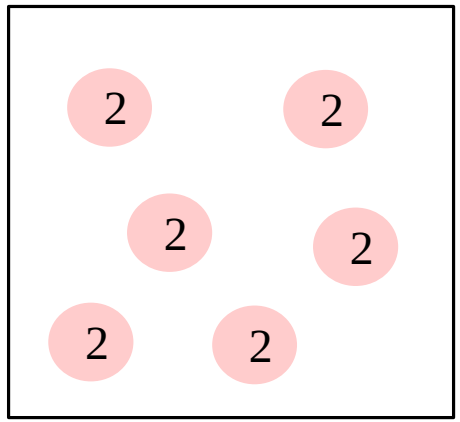


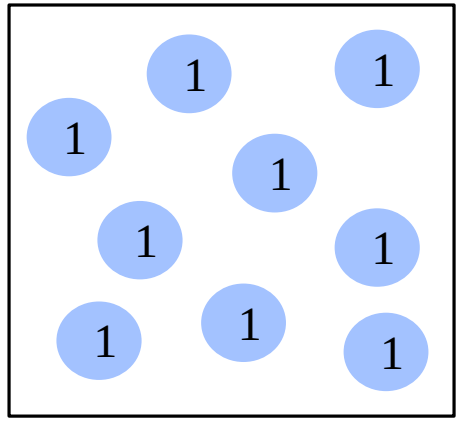
ε :energy parameter
σ :size parameter
k :binary parameter

Ensemble : *NVT*
Temperature : 88.3K
Temperature control : Nose method
Number of molecules: about 2000
Periodic boundary condition
Time step : 2 fs
Number of time steps : 1 - 4 × 10^6

q (interaction number) by molecular dynamics simulation(1)







$\varepsilon_{22} < \varepsilon_{11}$

$\rho_2 < \rho_1$

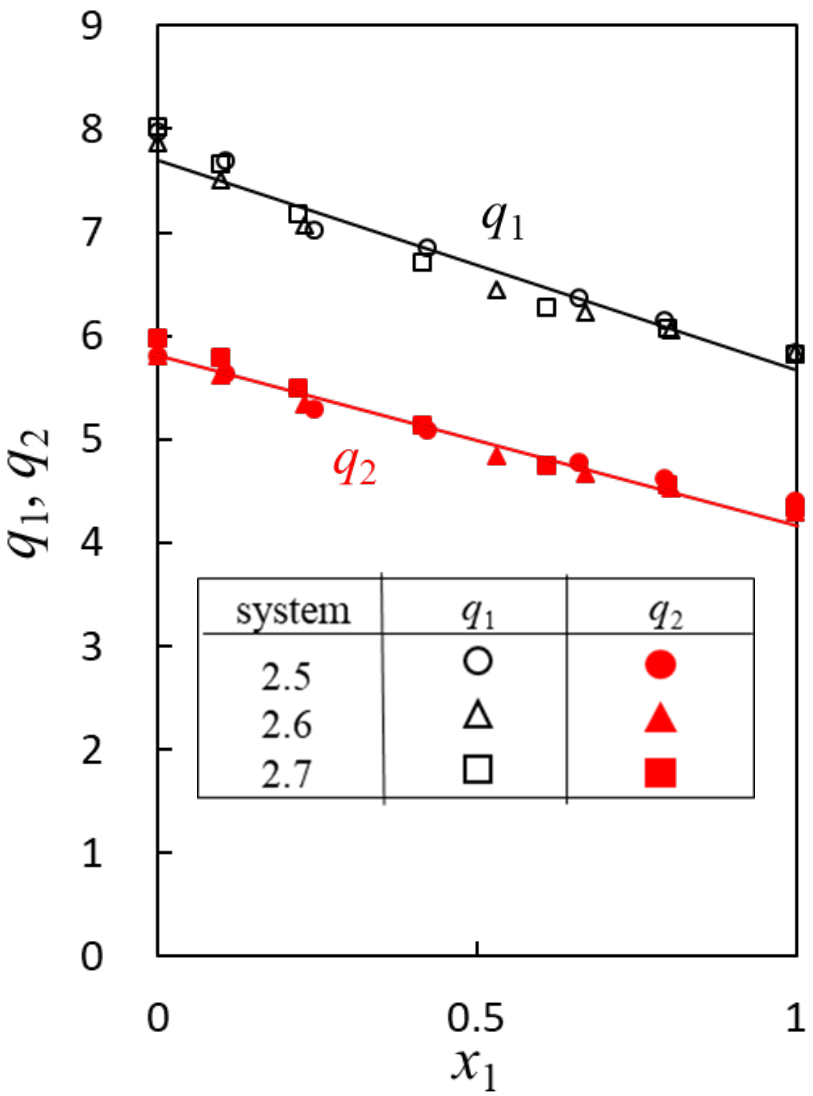
T=88.3 K

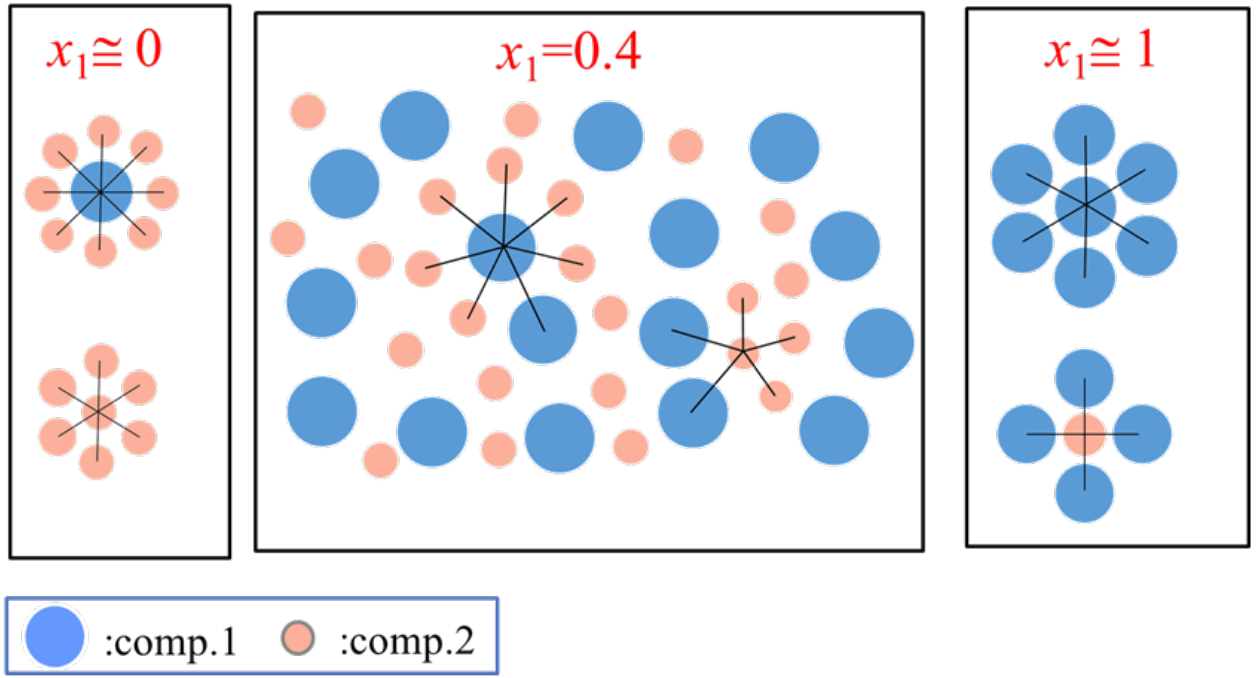
System	$\varepsilon_{11}/\varepsilon_{Ar}$	$\sigma_{11}^3/\sigma_{Ar}^3$	$\varepsilon_{22}/\varepsilon_{Ar}$	$\sigma_{22}^3/\sigma_{Ar}^3$	k_{12}
2.1	**1**	**1**	**0.75**	**1**	**0**
2.2	**1**	**1**	**0.75**	**1**	**0.05**
2.3	**1**	**1**	**0.75**	**1**	**0.1**
2.4	**1**	**1**	**0.75**	**1**	**-0.1**

ε_{Ar}/k =117.7 K, σ_{Ar}=3.401Å [1]

[1] http://dasher.wustl.edu/tinker/distribution/params/oplsaa.prm

q (interaction number) by molecular dynamics simulation(2)



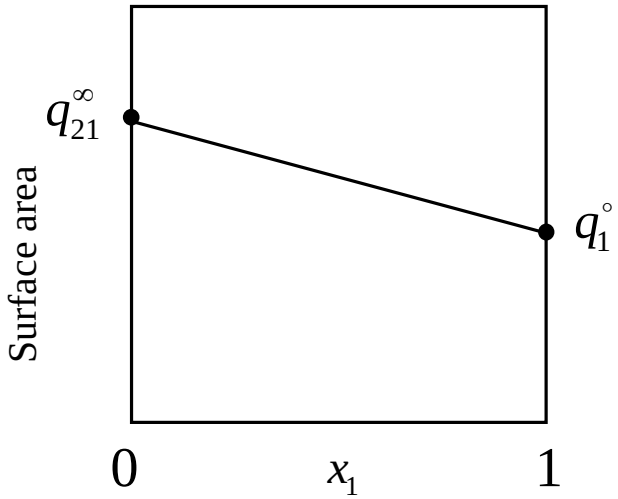


T=88.3 K

System	$\varepsilon_{11}/\varepsilon_{Ar}$	$\sigma_{11}^3/\sigma_{Ar}^3$	$\varepsilon_{22}/\varepsilon_{Ar}$	$\sigma_{22}^3/\sigma_{Ar}^3$	k_{12}
2.5	**1**	**1**	**1**	**0.5**	**0**
2.6	**1**	**1**	**1**	**0.5**	**0.1**
2.7	**1**	**1**	**1.07**	**0.5**	**0.1**

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Concentration dependent surface area parameter(CDSAP)model[1)]

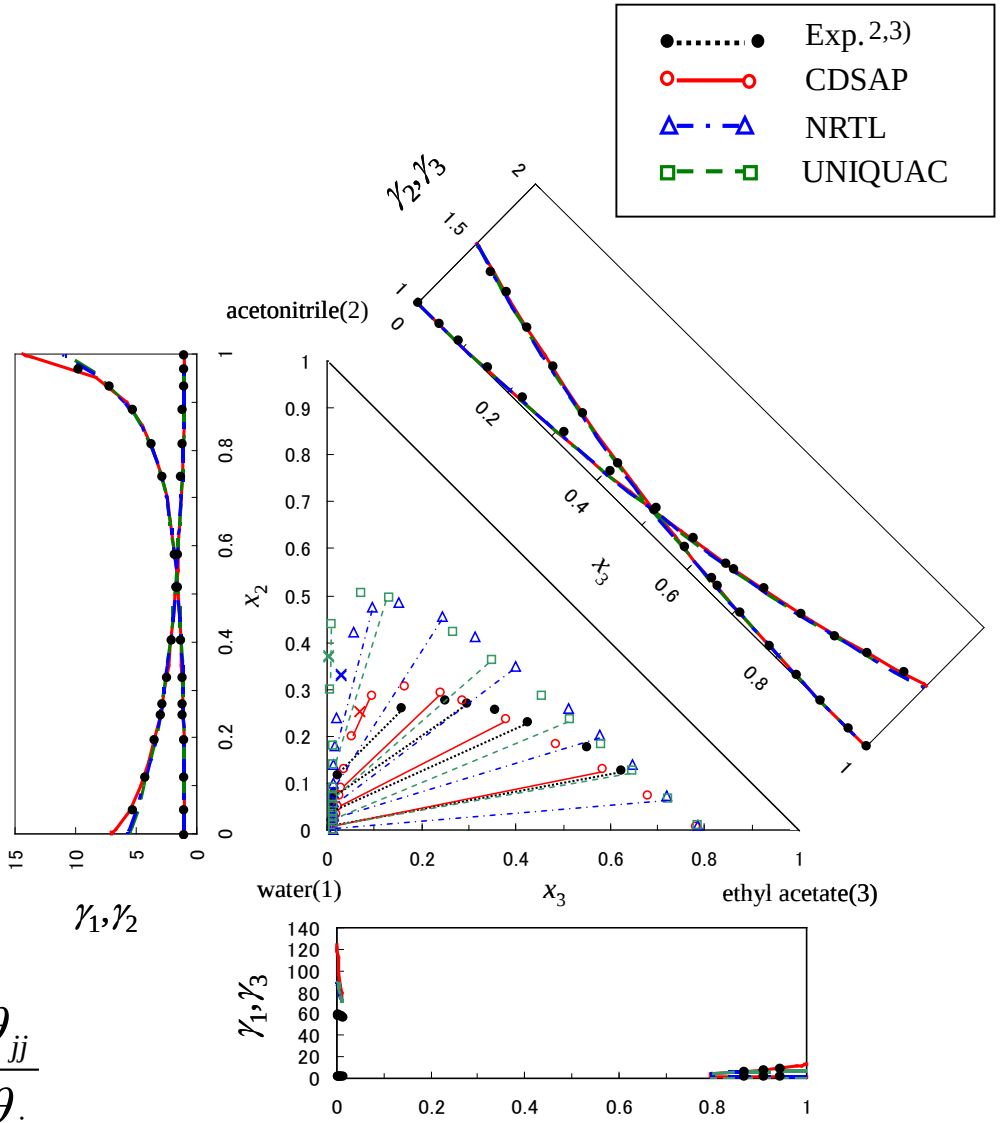


Surface area parameter q_1 for binary system.

$$q_i = q_i^{\circ} x_i + \sum_{j=1,\, j\neq i} q_{ji}^{\infty} x_j$$

$$G^{\mathrm{E}} = RT \sum_j q_j n_j \ln \frac{\theta_{jj}}{\theta_j} \qquad \ln \gamma_1 = \left[\frac{\partial G^{\mathrm{E}}}{RT \partial n_1} \right]_{T,P,n_2}$$

$$\ln \gamma_i = \left\{ q_i + \left(q_i^{\circ} - q_i \right) x_i \right\} \ln \frac{\theta_{ii}}{\theta_i} + \sum_{j=1,\, j\neq i} \left(q_{ij}^{\infty} - q_j \right) x_j \ln \frac{\theta_{jj}}{\theta_j}$$



Water (1) + acetonitrile (2) + ethyl acetate(3) system at 60°C

[1] Y.Iwai,Y.Yamamoto, Fluid Phase Equilibria,337 (2013) 165-173.
[2] A. N. Campbell, S. C. Anand, Canadian J. Chem. 50 (1972) 479-489.
[3] S. E. Kharin, V. M. Perelygin, A.G. Volkov, Izv. Vyssh. Uchebn. Zaved. Pishch. Tekhnol. 4 (1968) 136-139.

Taylor series at $\Delta E_{12}=0$ for G^{E}

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \qquad \theta_2 = 1 - \theta_1 \qquad \frac{\theta_{12}\theta_{21}}{\theta_{11}\theta_{22}} = \tau_{12} = \exp(\Delta E_{12}) \qquad \Delta E_{12} = \frac{2u_{12} - u_{11} - u_{22}}{kT} = \frac{2E_{12} - E_{11} - E_{22}}{RT}$$

$$E_{ij} = u_{ij} N_A$$

$$G^{E}(\Delta E_{12}) = RT\left(q_1 n_1 \ln\frac{\theta_{11}}{\theta_1} + q_2 n_2 \ln\frac{\theta_{22}}{\theta_2} \right)$$

Sum of first 2 terms of Taylor series at $\Delta E_{12}=0$ (Maclaurin series)

$$G^{E}(\Delta E_{12}) \cong G^{E}(0) + \frac{dG^{E}(0)}{d\Delta E_{12}} \Delta E_{12}$$

$$= RT\left\{ q_1 n_1 (-\Delta E_{12}) \theta_2^{\,2} + q_2 n_2 (-\Delta E_{12}) \theta_1^{\,2} \right\}$$

$$= -RT\Delta E_{12} \frac{q_1 n_1 \, q_2 n_2}{(q_1 n_1 + q_2 n_2)}$$

$$\therefore G_m^{E} = -RT\Delta E_{12} \frac{q_1 x_1 \, q_2 x_2}{(q_1 x_1 + q_2 x_2)}$$

Regular solution theory

$$G_m^{E} = (\delta_1 - \delta_2)^2 \frac{V_{m,1} x_1 \, V_{m,2} x_2}{(V_{m,1} x_1 + V_{m,2} x_2)}$$

$-RT\Delta E_{12}$ $\longleftrightarrow$ $(\delta_1 - \delta_2)^2$

q_i $\longleftrightarrow$ $V_{m,i}$

Activity coefficients of binary system for new model

$$G^{\mathrm{E}} = -RT\Delta E_{12}\frac{q_1 n_1\, q_2 n_2}{(q_1 n_1 + q_2 n_2)}$$

q_i depends on concentration

$$q_1 = q_1^{\,0} x_1 + q_{21}^{\,\infty} x_2 \qquad q_2 = q_2^{\,0} x_2 + q_{12}^{\,\infty} x_1$$

$$\ln\gamma_1 = \left[\frac{\partial G^{\mathrm{E}}}{RT\partial n_1}\right]_{T,P,n_2}$$

$$= -\Delta E_{12}\left[\left\{q_1^{\,0} + \left(q_{21}^{\,\infty} - q_1^{\,0}\right)x_2^2\right\}\theta_2^2 + \left(q_{12}^{\,\infty} - q_2^{\,0}\right)x_2^2\theta_1^2\right]$$

$$-q_1^{\,0}\Delta E_{12} = c_{21}^{\,0}$$
$$-q_2^{\,0}\Delta E_{12} = c_{12}^{\,0}$$
$$-q_{21}^{\,\infty}\Delta E_{12} = c_{21}^{\,\infty}$$
$$-q_{12}^{\,\infty}\Delta E_{12} = c_{12}^{\,\infty}$$

Binary parameters

NOT pure component parameters

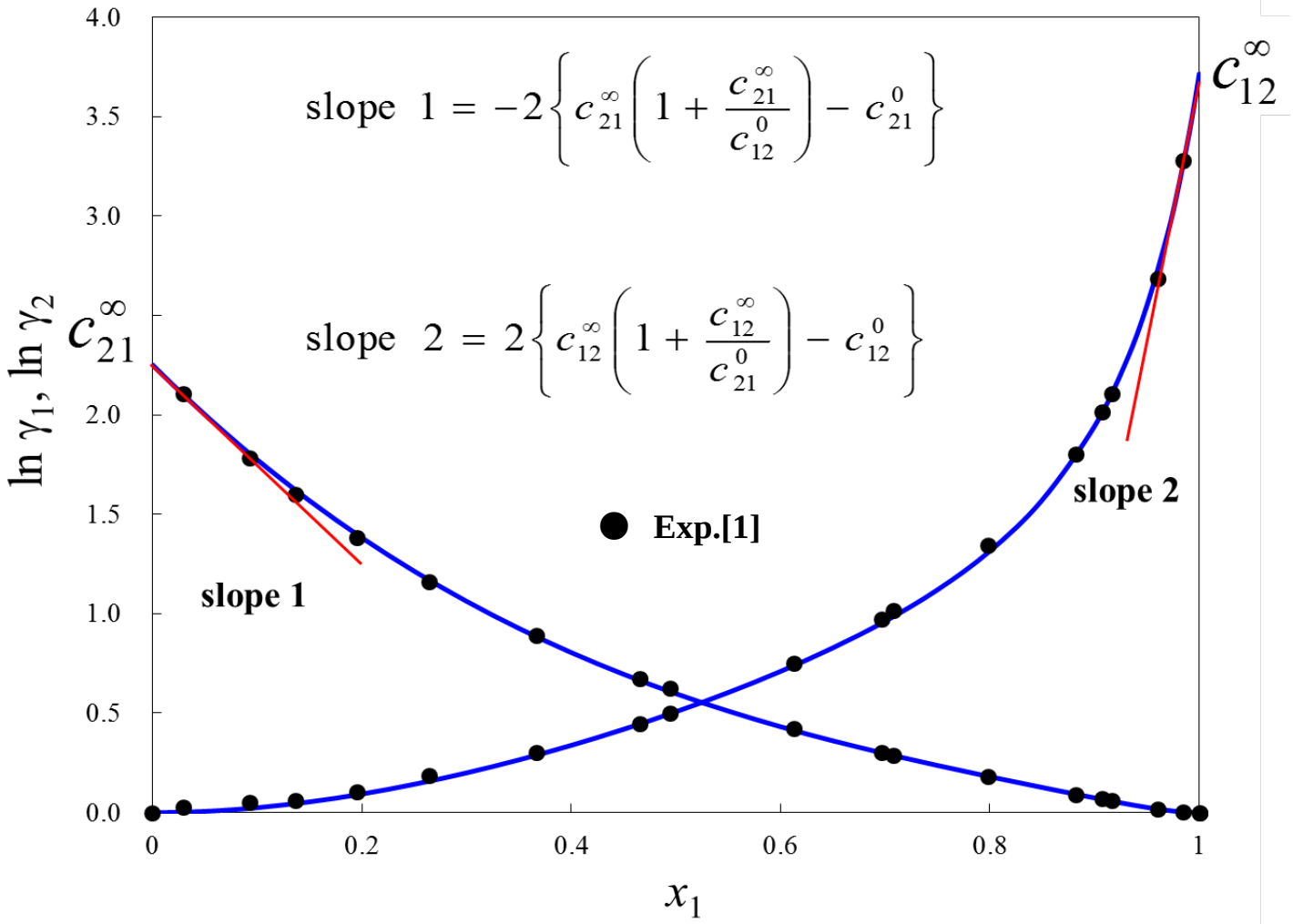
$$\theta_1 = \frac{c_1 x_1}{c_1 x_1 + c_2 x_2}, \quad \theta_2 = 1 - \theta_1$$

$$c_1 = c_{21}^{\,0} x_1 + c_{21}^{\,\infty} x_2$$
$$c_2 = c_{12}^{\,0} x_2 + c_{12}^{\,\infty} x_1$$

$$\ln\gamma_1 = \left\{c_{21}^{\,0} + \left(c_{21}^{\,\infty} - c_{21}^{\,0}\right)x_2^2\right\}\theta_2^2 + \left(c_{12}^{\,\infty} - c_{12}^{\,0}\right)x_2^2\theta_1^2$$

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Physical meanings of parameters (Hexane(1)+Ethanol(2) at 40 ℃)



$$\ln\gamma_1^{\infty} = c_{21}^{\infty}$$

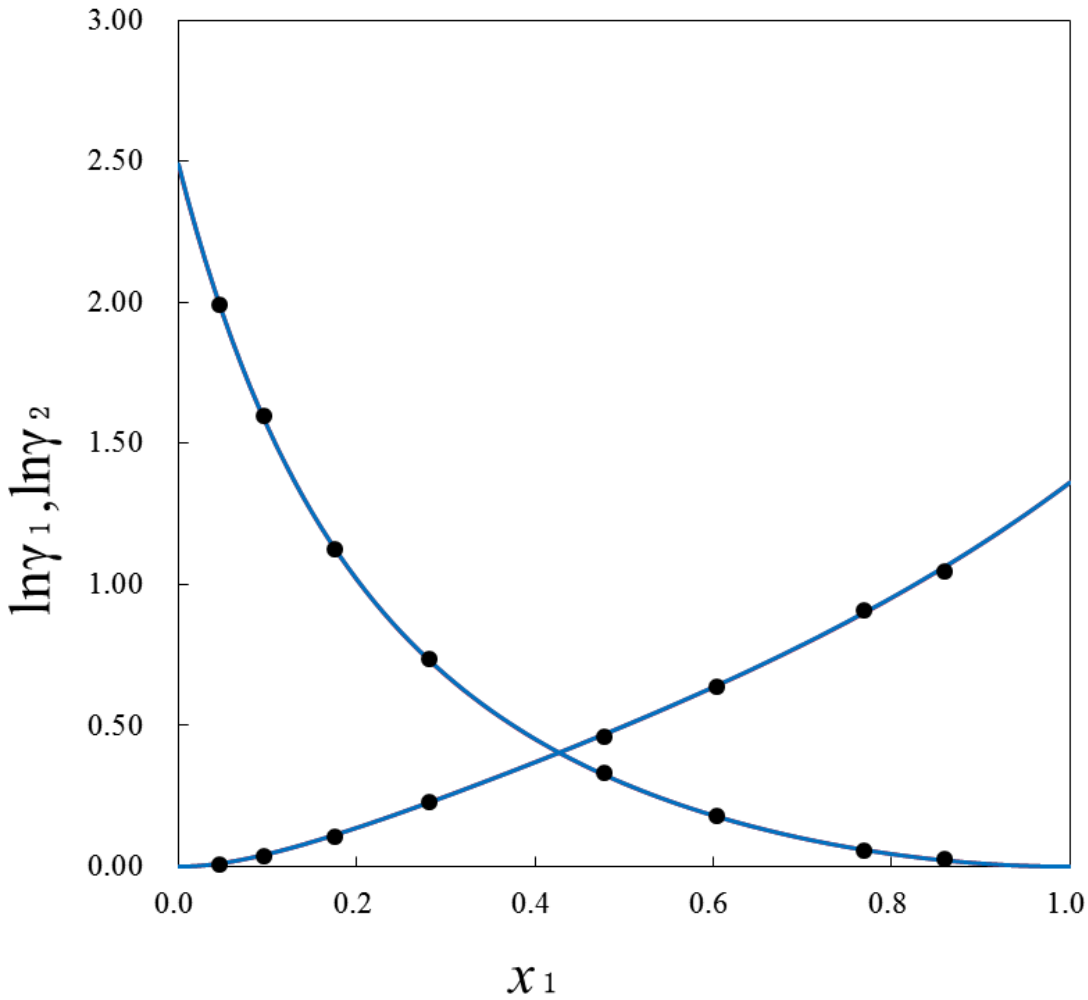
$$\ln\gamma_2^{\infty} = c_{12}^{\infty}$$

c^{0}_{21}	c^{0}_{12}	c^{∞}_{21}	c^{∞}_{12}
0.791	**4.368**	**2.252**	**3.715**

[1] H. Sugi, T. Katayama, J. Chem. Eng. Jpn 11 (1978) 167-172.

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2-Propanol (1) + water(2) system at 45.05 ℃



●:Experimental data [1]
:New model,
:NRTL

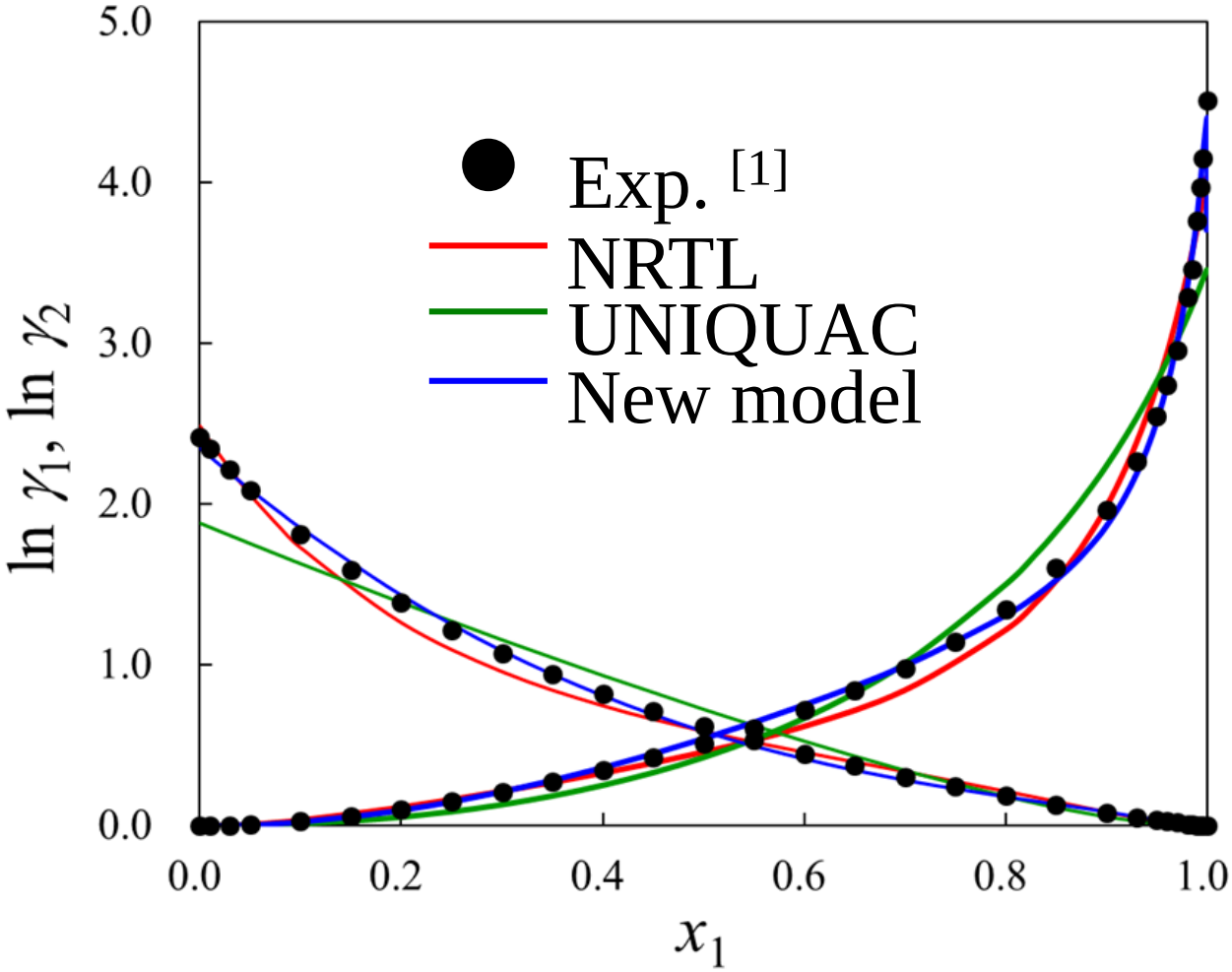
Correlated results by two models are overlapped.

NRTL		
τ_{12}	τ_{21}	α
0.665	2.019	0.527

New model			
c^{0}_{21}	c^{0}_{12}	c^{∞}_{21}	c^{∞}_{12}
2.095	1.065	2.490	1.362

[1] E. Sada; T. Morisue: J. Chem. Eng. Jpn., .8,191(1975)

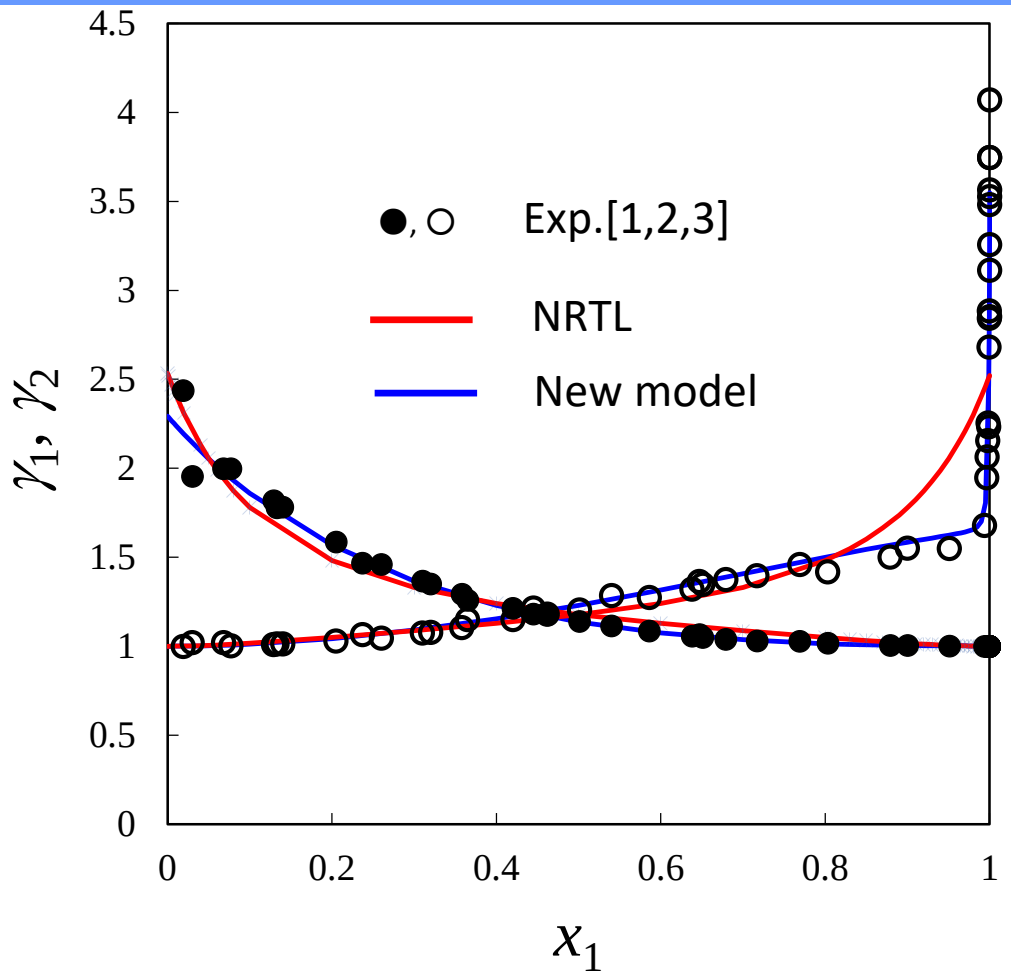
Hexane(1)+ethanol(2) at 10 °C

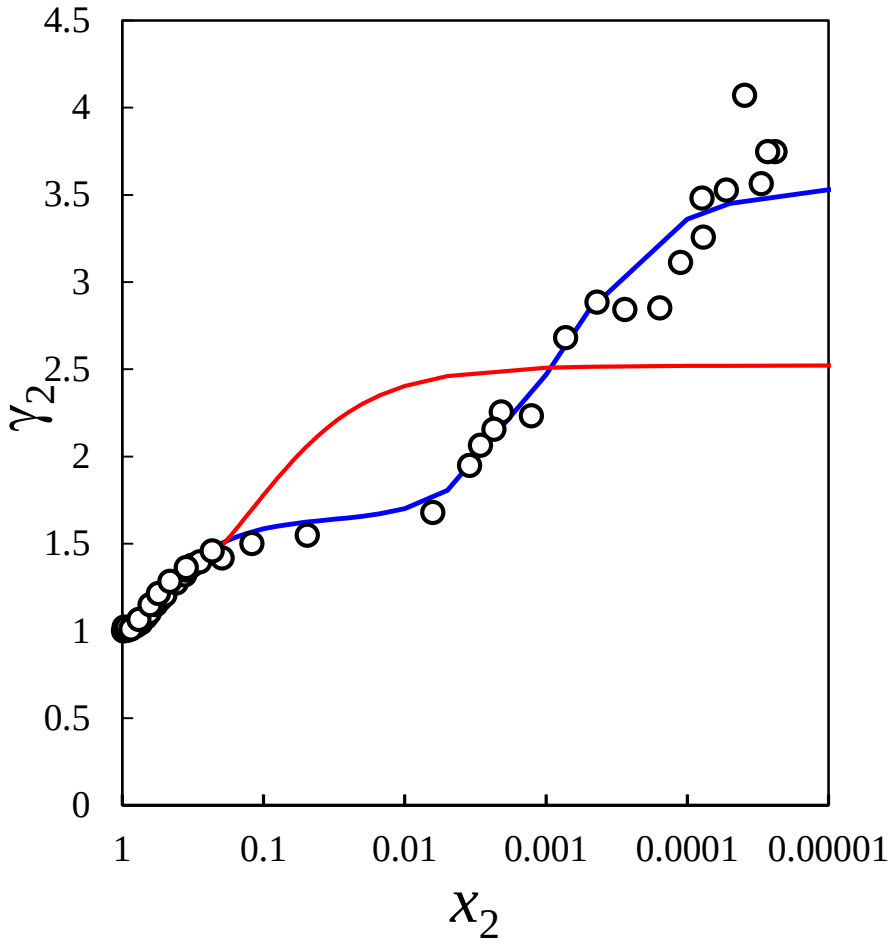


New model	c_{21}^0	c_{12}^0	c_{21}^∞	c_{12}^∞
	0.524	6.337	2.352	4.413
NRTL	τ_{12}	τ_{21}	α_{12}	
	3.310	1.862	0.5029	
UNIQUAC	τ_{12}	τ_{21}		
	0.163	1.065		

[1] S. J. O'Shea, R. H. Stokes, J. Chem. Thermodyn., 18, 691(1986)

Methanol(1)+Water at 0.1 MPa





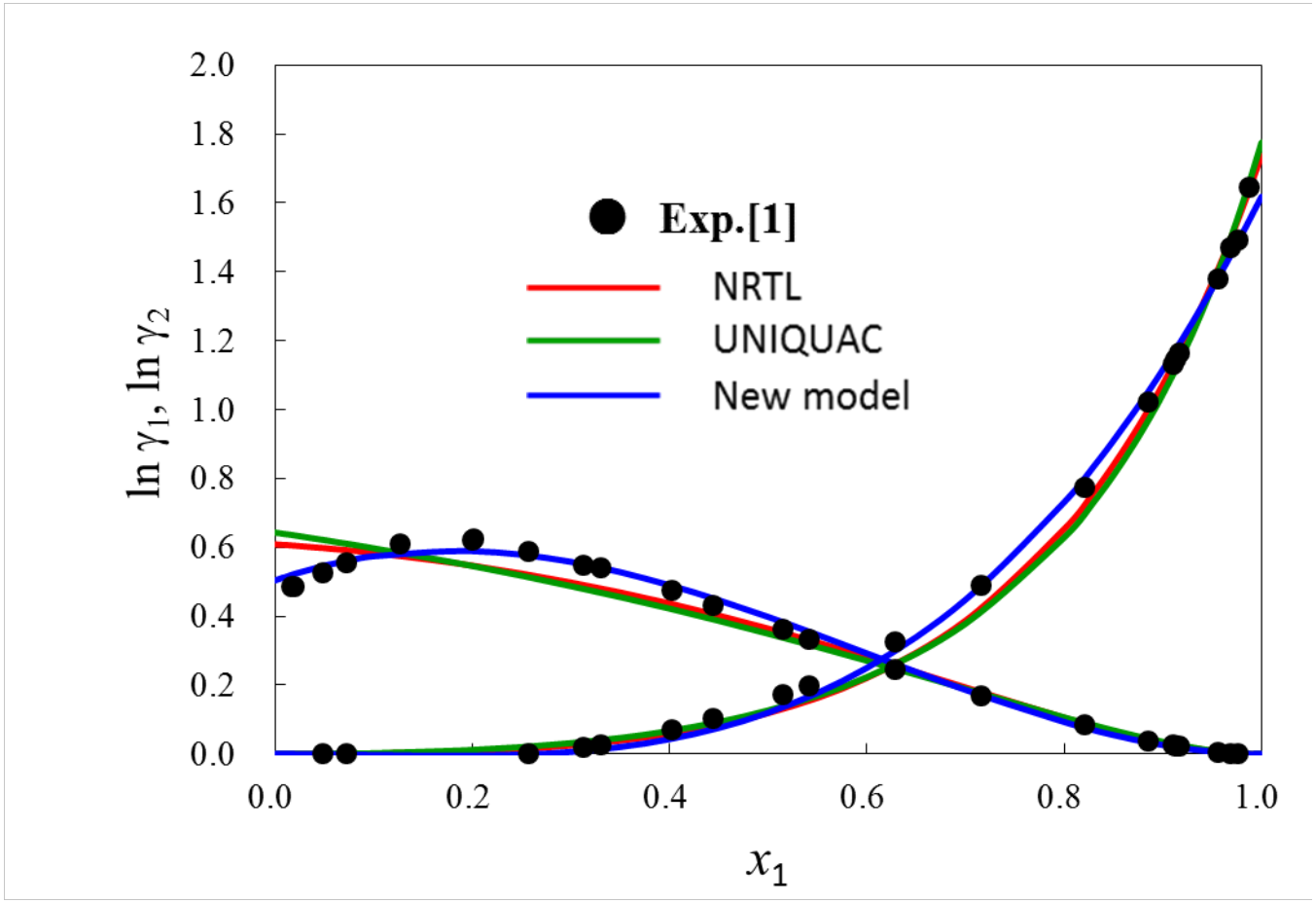
NRTL		
τ_{12}	τ_{21}	α
0.767	**0.087**	**0.3**

New model			
c^0_{21}	c^0_{12}	c^∞_{21}	c^∞_{12}
0.0055	**2.12**	**0.8296**	**1.267**

[1] M. KATO, H. KONISHI, M. HIRATA, J. Chem. Eng. Data 15 (1970) 501-505. [2] A. Ikari, Y. Hatate, M. Futai, Y. Kurokawa, J. Chem. Eng. Data 30 (1985) 163-165. [3] K. Kurihara, M. Nakamichi, K. Kojima, J. Chem. Eng. Data 38 (1993) 446-449.

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Chloroform (1) + Ethanol (2) at 45 °C



NRTL		
τ_{12}	τ_{21}	α
2.389	-0.552	0.302

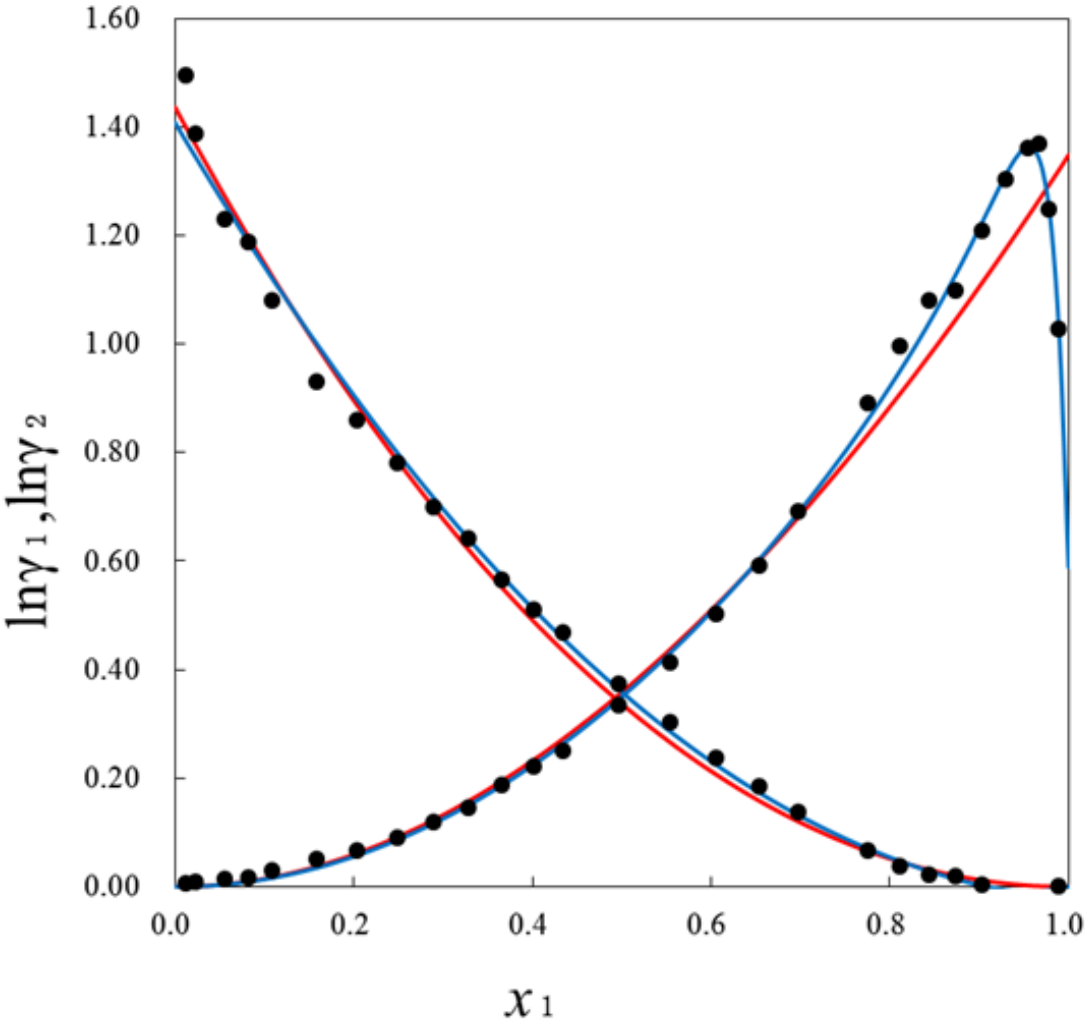
UNIQUAC	
τ_{12}	τ_{21}
0.199	1.722

New model			
c^{0}_{21}	c^{0}_{12}	c^{∞}_{21}	c^{∞}_{12}
1.467	0.56	0.504	1.619

[1] G. Scatchard, C. L. Raymond, J. Am. Chem. Soc. 60 (1938) 1278-1287.

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Methanol (1) + vinyl acetate (2) at 60 ℃



●:Experimental data [1]

:New model,

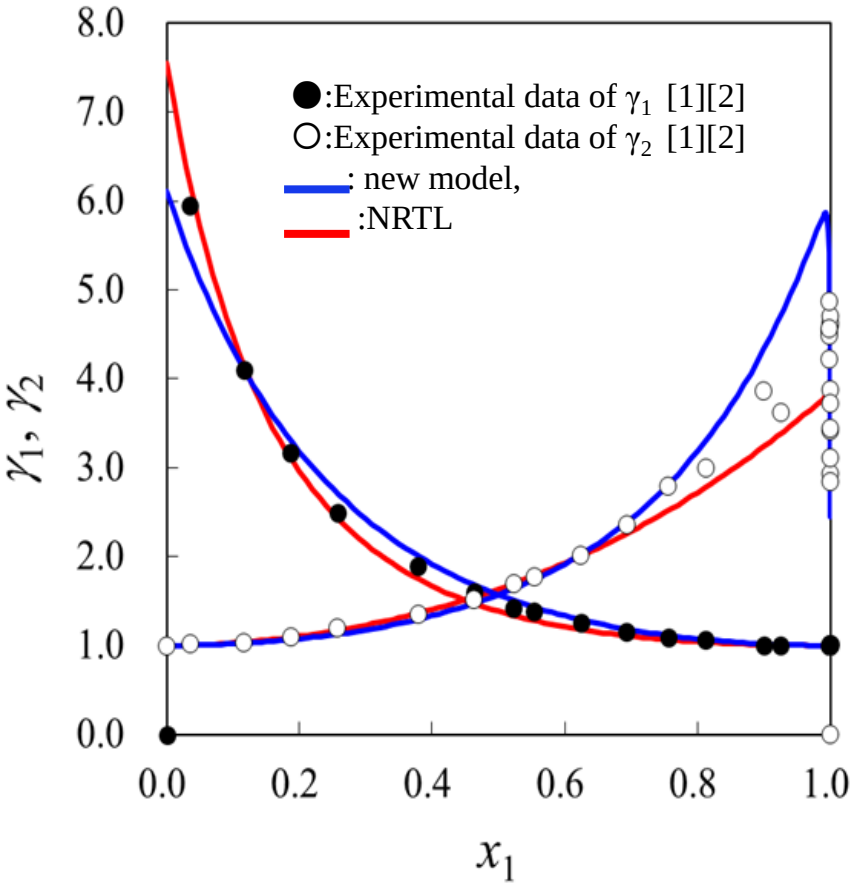
:NRTL

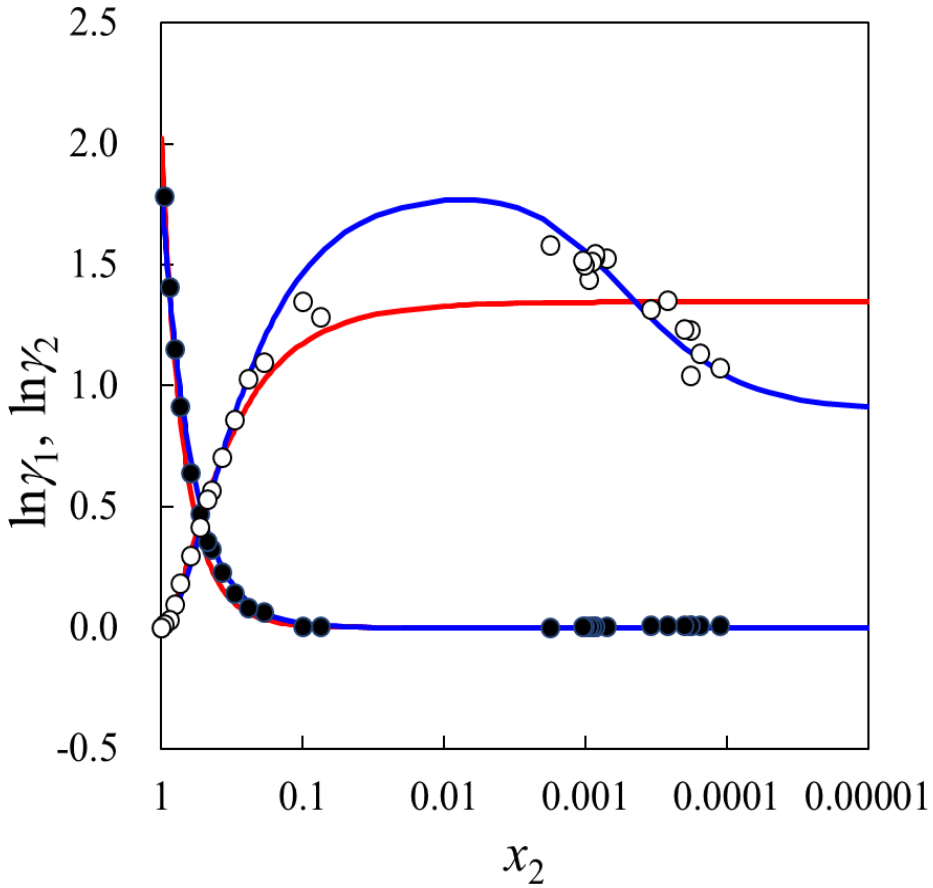
[1] Confident. Comp. Res. Rep. LC5320(1979)

NRTL		
τ_{12}	τ_{21}	α
-0.753	2.201	0.021

New model			
c^{0}_{21}	c^{0}_{12}	c^{∞}_{21}	c^{∞}_{12}
0.077	30.993	1.407	0.589

1,4-Dioxane (1) + water (2) at 70&101 ℃



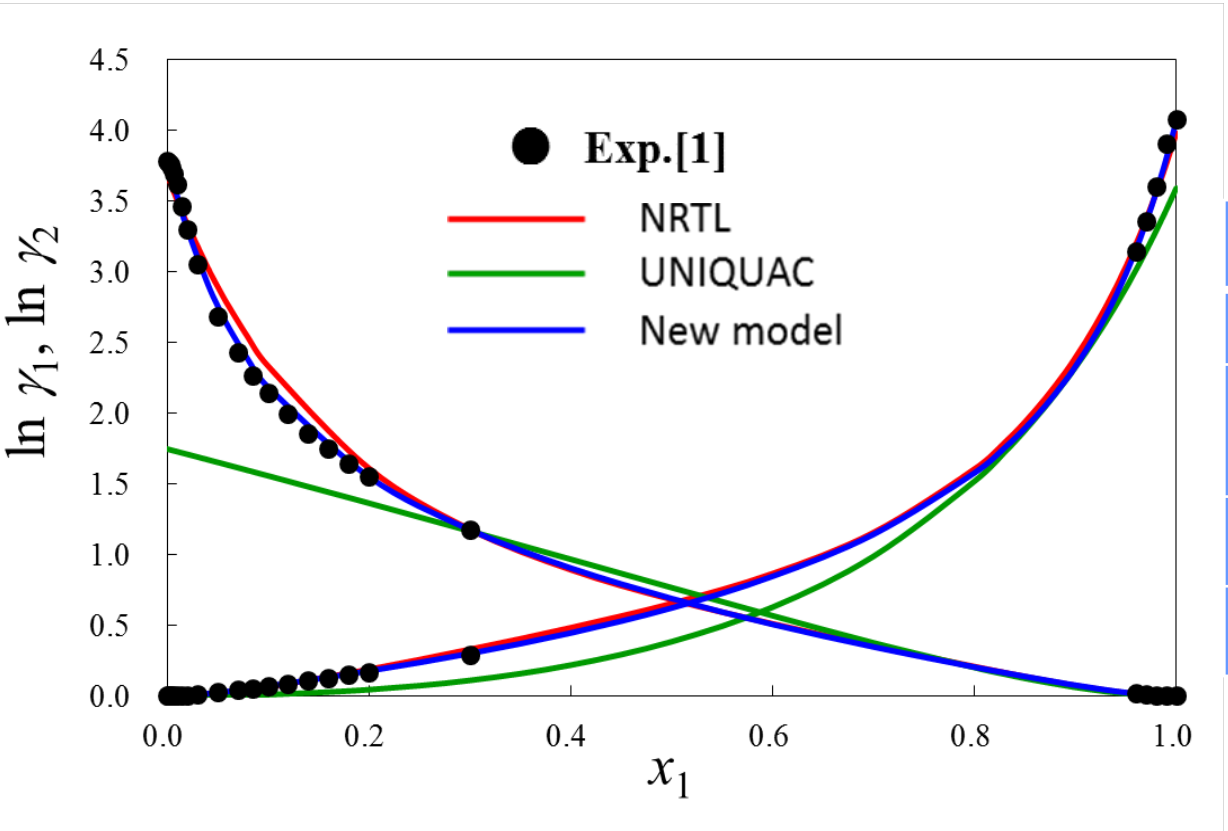


NRTL		
τ_{12}	τ_{21}	α
-1.862	4.103	0.060

New model			
c^0_{21}	c^0_{12}	c^∞_{21}	c^∞_{12}
0.001	1662.8	1.809	0.894

[1] G. Kortuem; V. Valent: Ber. Bunsenges. Phys. Chem.,81,752(1977), [2] A. Ikari; Y. Hatae; M. Futai: J. Chem. Data,30,163(1985)

Ethanol (1) + hexadecane (2) system at 25 °C



Liquid-liquid equilibria

		Calculated results		
	Data [1]	New model	NRTL	UNIQUAC
x_1^{I}	0.315	0.315	0.315	0.307
x_1^{II}	0.957	0.959	0.960	0.963

NRTL		
τ_{12}	τ_{21}	α
3.111	2.838	0.415

UNIQUAC	
τ_{12}	τ_{21}
1.133	0.242

New model			
c^{0}_{21}	c^{0}_{12}	c^{∞}_{21}	c^{∞}_{12}
1.447	1.172	3.814	4.071

[1] H. T. French, A. Richards, R. H. Stokes, J. Chem. Thermodyn. 11 (1979) 671-686.

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Gibbs-Helmholtz eq. and temperature dependent parameters

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = \sum_i x_i \ln\gamma_i$$

$$\left(\frac{\partial\left(G_{\mathrm{m}}^{\mathrm{E}}/T\right)}{\partial(1/T)}\right)_{p,n} = h_{\mathrm{m}}^{\mathrm{E}}$$

$G_{\mathrm{m}}^{\mathrm{E}}$: Excess molar Gibbs energy
$h_{\mathrm{m}}^{\mathrm{E}}$: Excess molar enthalpy
R : Gas constant
T : Temperature
p : Pressure
n : Amount of substance

$$c_{ij}^{0} = A_{ij}^{0} + \frac{B_{ij}^{0}}{T} \qquad c_{ij}^{\infty} = A_{ij}^{\infty} + \frac{B_{ij}^{\infty}}{T}$$

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = (c_1x_1 + c_2x_2)\theta_1\theta_2$$

$$h_{\mathrm{m}}^{\mathrm{E}} = R\left(\frac{c_1{}'}{c_1}\theta_2 + \frac{c_2{}'}{c_2}\theta_1\right)\frac{c_1x_1c_2x_2}{c_1x_{1+}c_2x_2}$$

$$\theta_1 = \frac{c_1x_1}{c_1x_1+c_2x_2},\ \theta_2 = 1-\theta_1$$

$$c_1 = c_{21}^{\circ}x_1 + c_{21}^{\infty}x_2$$

$$c_2 = c_{12}^{\circ}x_2 + c_{12}^{\infty}x_1$$

$$c_1{}' = B_{21}^{\circ}x_1 + B_{21}^{\infty}x_2$$

$$c_2{}' = B_{12}^{\circ}x_2 + B_{12}^{\infty}x_1$$

Correlated results of chloroform(1) + ethanol(2) system

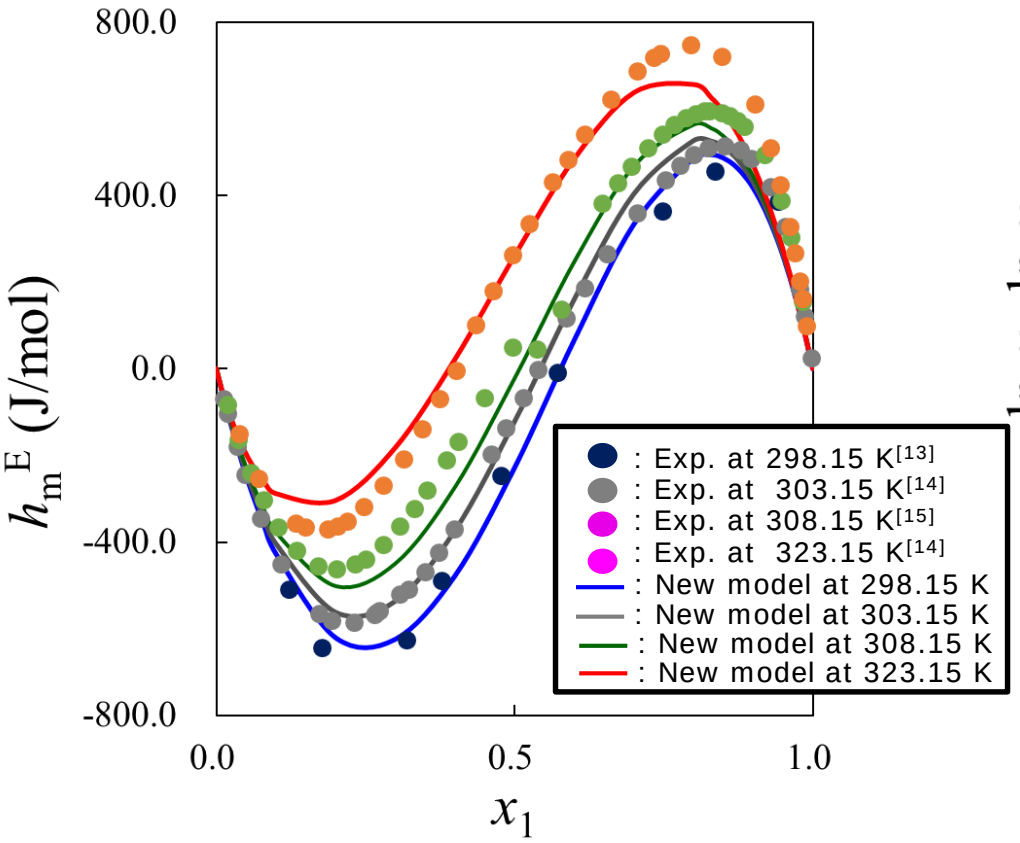


Fig. Heat of mixing for chloroform(1) + ethanol(2)

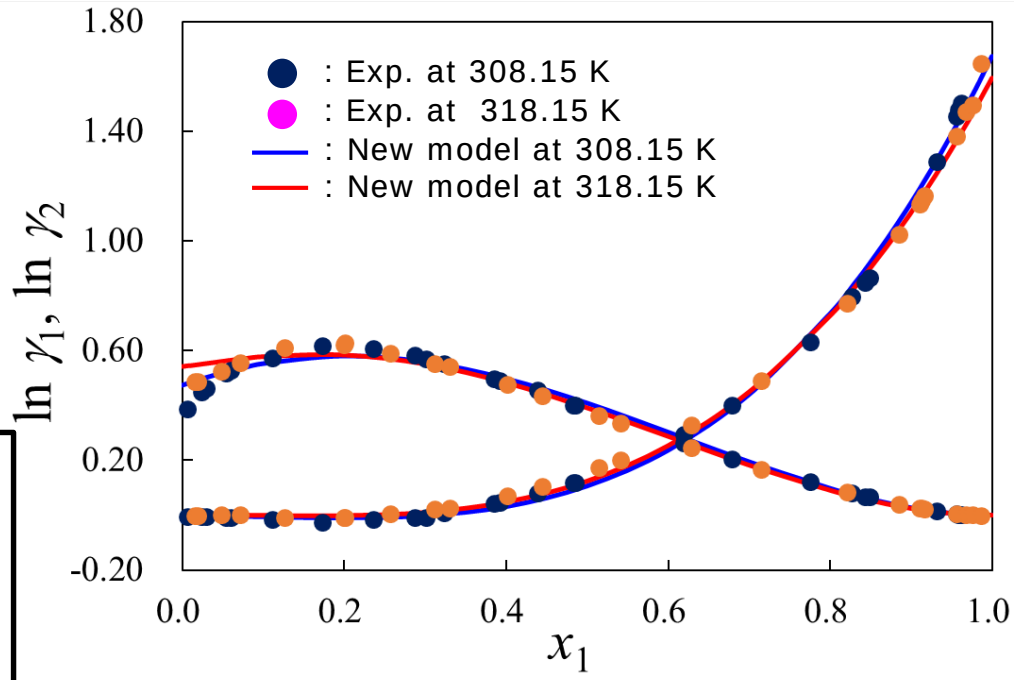


Fig. Activity coefficients for chloroform(1) + ethanol(2)[12]

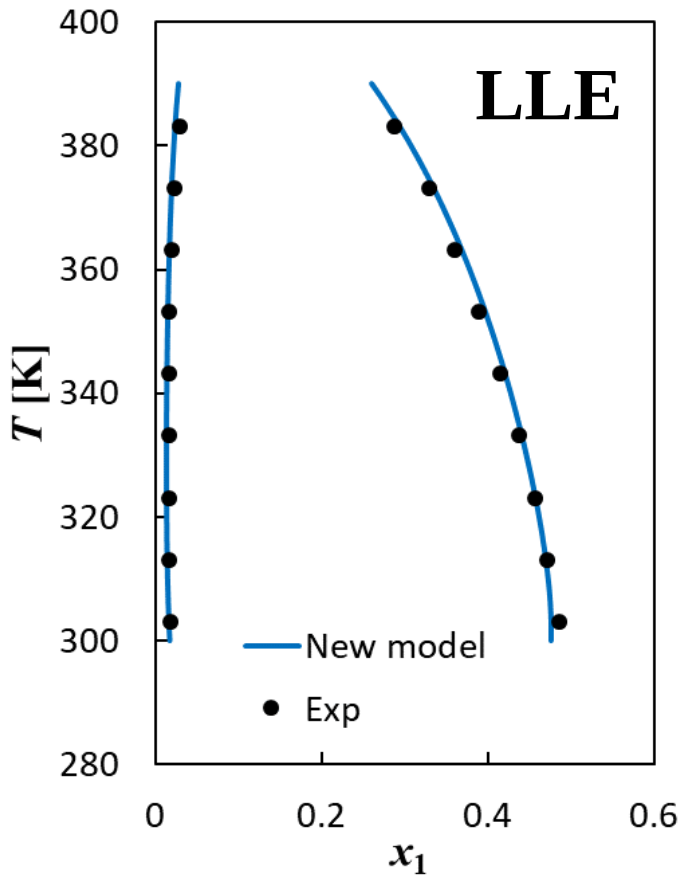
$$c_{ij}^0 = A_{ij}^0 + \frac{B_{ij}^0}{T} \quad , \quad c_{ij}^\infty = A_{ij}^\infty + \frac{B_{ij}^\infty}{T}$$

A_{21}^0	B_{21}^0 [K]	A_{12}^0	B_{12}^0 [K]
-804.626	4.271	496.181	-1.280

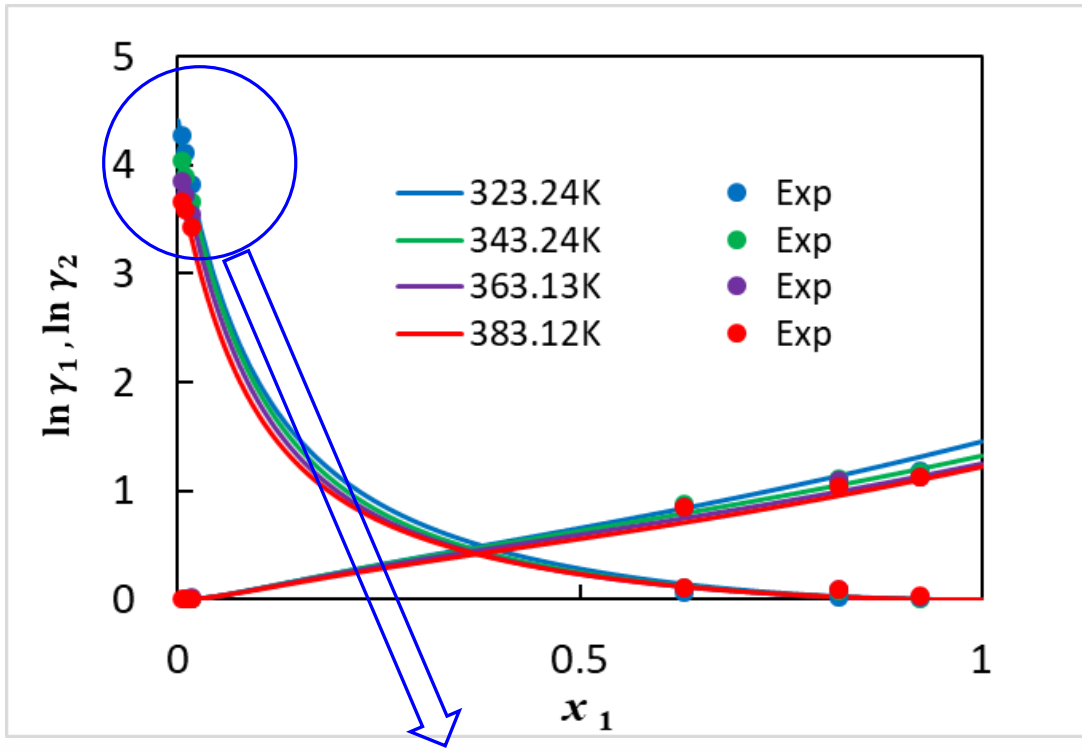
A_{21}^∞	B_{21}^∞ [K]	A_{12}^∞	B_{12}^∞ [K]
-677.005	2.671	771.773	-0.832

[12] Scatchard, G. and Raymond, C.L., J. Am. Chem. Soc., **60**(6), 1278
[13] Hirobe. H, J. Fac. Sci., Imp. Univ. Tokyo **1**, 155(1926)
[14] Shatas J. P., Abbott M. M., Van ness H. C., J. Chem. Eng. Data **20**, 406(1975)
[15] Nagata I., Kawamura Y., Asano H., Fujiwara K., Z. Phys. Chem. (Leipzig) **259**, 1109(1978)

Correlated results of 1-butanol(1) + water(2) system

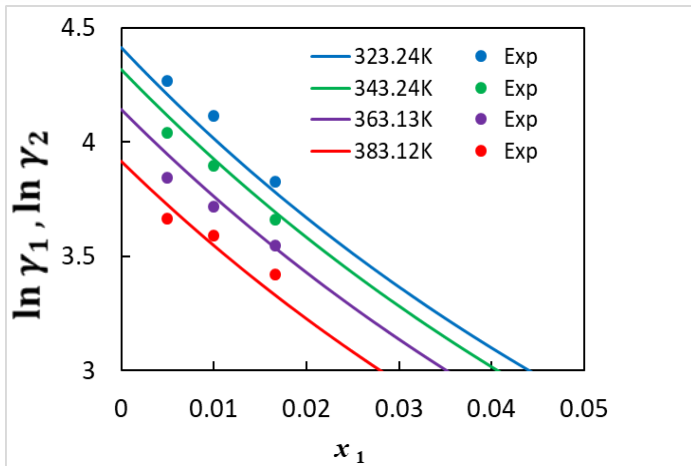


VLE



$$c_{ij}^{0} = A_{ij}^{0} + \frac{B_{ij}^{0}}{T} + \frac{C_{ij}^{0}}{T^2} \qquad c_{ij}^{\infty} = A_{ij}^{\infty} + \frac{B_{ij}^{\infty}}{T} + \frac{C_{ij}^{\infty}}{T^2}$$

ij	A^{0}_{ij}	B^{0}_{ij} (K)	C^{0}_{ij} (K^2)	A^{∞}_{ij}	B^{∞}_{ij} (K)	C^{∞}_{ij} (K^2)
21	29.832	-7927	482508	-12.275	10565	-1671459
12	-3.6817	2665	-401123	6.4335	-4091	801939



Activity coefficient for ternary system

$$G^{\mathrm{E}} = -RT\left(q_1 n_1 + q_2 n_2 + q_3 n_3\right)\left\{\Delta E_{12}\theta_1\theta_2 + \Delta E_{23}\theta_2\theta_3 + \Delta E_{31}\theta_3\theta_1\right\}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad q_i = q_i^{\,0} x_i + \sum_{j\neq i} q_{ji}^{\,\infty} x_j$$

$$\ln\gamma_1 = \left[\frac{\partial G^{\mathrm{E}}}{RT\partial n_1}\right]_{T,p,n_2,n_3}$$

$$= c_{21}^{\,0}\left\{\frac{q_1}{q_1^{\,0}}(1-x_1)+x_1\right\}\times\left[\theta_2(1-\theta_1)-\frac{\Delta E_{23}}{\Delta E_{12}}\theta_2\theta_3+\frac{\Delta E_{31}}{\Delta E_{12}}\theta_3(1-\theta_1)\right]$$

$$+ c_{21}^{\,0}\left\{\frac{c_{12}^{\,\infty}}{c_{21}^{\,0}}-\frac{q_2}{q_1^{\,0}}\right\}x_2\times\left[\theta_1(1-\theta_2)-\frac{\Delta E_{23}}{\Delta E_{12}}\theta_3(1-\theta_2)-\frac{\Delta E_{31}}{\Delta E_{12}}\theta_1\theta_3\right]$$

$$+ c_{21}^{\,0}\left\{\frac{c_{13}^{\,\infty}}{c_{31}^{\,0}}-\frac{q_3}{q_1^{\,0}}\right\}x_3\times\left[-\theta_1\theta_2+\frac{\Delta E_{23}}{\Delta E_{12}}\theta_2(1-\theta_3)+\frac{\Delta E_{31}}{\Delta E_{12}}\theta_1(1-\theta_3)\right]$$

$$\theta_i = \frac{\left(q_i/q_1^{\,0}\right)x_i}{\sum_j\left(q_j/q_1^{\,0}\right)x_j} \qquad \frac{q_j}{q_1^{\,0}} = \frac{c_{1j}^{\,0}}{c_{j1}^{\,0}}\sum_k \frac{c_{kj}^{\,\infty}}{c_{kj}^{\,0}}x_k \qquad \frac{c_{kk}^{\,\infty}}{c_{kk}^{\,0}} = 1$$

$$c_{ji}^{\,0} = -q_i^{\,0}\Delta E_{ji}$$

$$c_{ji}^{\,\infty} = -q_{ji}^{\,\infty}\Delta E_{ji}$$

parameters

$$\frac{\Delta E_{23}}{\Delta E_{12}} = \frac{c_{32}^{\,0}}{c_{12}^{\,0}}, \qquad \frac{\Delta E_{31}}{\Delta E_{12}} = \frac{c_{31}^{\,0}}{c_{21}^{\,0}}$$

$$\Delta E_{ji} = \Delta E_{ij}$$

restriction condition

$$\frac{q_2^{\,0}}{q_1^{\,0}}\frac{q_1^{\,0}}{q_3^{\,0}}\frac{q_3^{\,0}}{q_2^{\,0}} = 1 \quad \therefore \frac{c_{12}^{\,0}}{c_{21}^{\,0}}\frac{c_{31}^{\,0}}{c_{13}^{\,0}}\frac{c_{23}^{\,0}}{c_{32}^{\,0}} = 1$$

Number of fitting parameters are
(4/binary system)×(3 binary systems)
- (1 restriction condition)
=11 for a ternary system.

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Parameters for ternary system

$$(1)+(2);\quad -q_1^0\Delta E_{12}=c_{21}^0,\ -q_2^0\Delta E_{12}=c_{12}^0,\ -q_{21}^\infty\Delta E_{12}=c_{21}^\infty,\ -q_{12}^\infty\Delta E_{12}=c_{12}^\infty$$

$$(2)+(3);\quad -q_2^0\Delta E_{23}=c_{32}^0,\ -q_3^0\Delta E_{23}=c_{23}^0,\ -q_{32}^\infty\Delta E_{23}=c_{32}^\infty,\ -q_{23}^\infty\Delta E_{23}=c_{23}^\infty$$

$$(3)+(1);\quad -q_1^0\Delta E_{31}=c_{31}^0,\ -q_3^0\Delta E_{31}=c_{31}^0,\ -q_{31}^\infty\Delta E_{31}=c_{31}^\infty,\ -q_{13}^\infty\Delta E_{31}=c_{13}^\infty$$

Same (Number of parameters = 11)

$c_{21}^0,\ c_{12}^0,\ c_{21}^\infty,\ c_{12}^\infty$

$c_{31}^0,\ c_{13}^0,\ c_{31}^\infty,\ c_{13}^\infty$

$c_{32}^0,\ c_{23}^0,\ c_{32}^\infty,\ c_{23}^\infty$

restriction condition

$$\frac{c_{12}^{\ 0}}{c_{21}^{\ 0}}\frac{c_{31}^{\ 0}}{c_{13}^{\ 0}}\frac{c_{23}^{\ 0}}{c_{32}^{\ 0}}=1$$

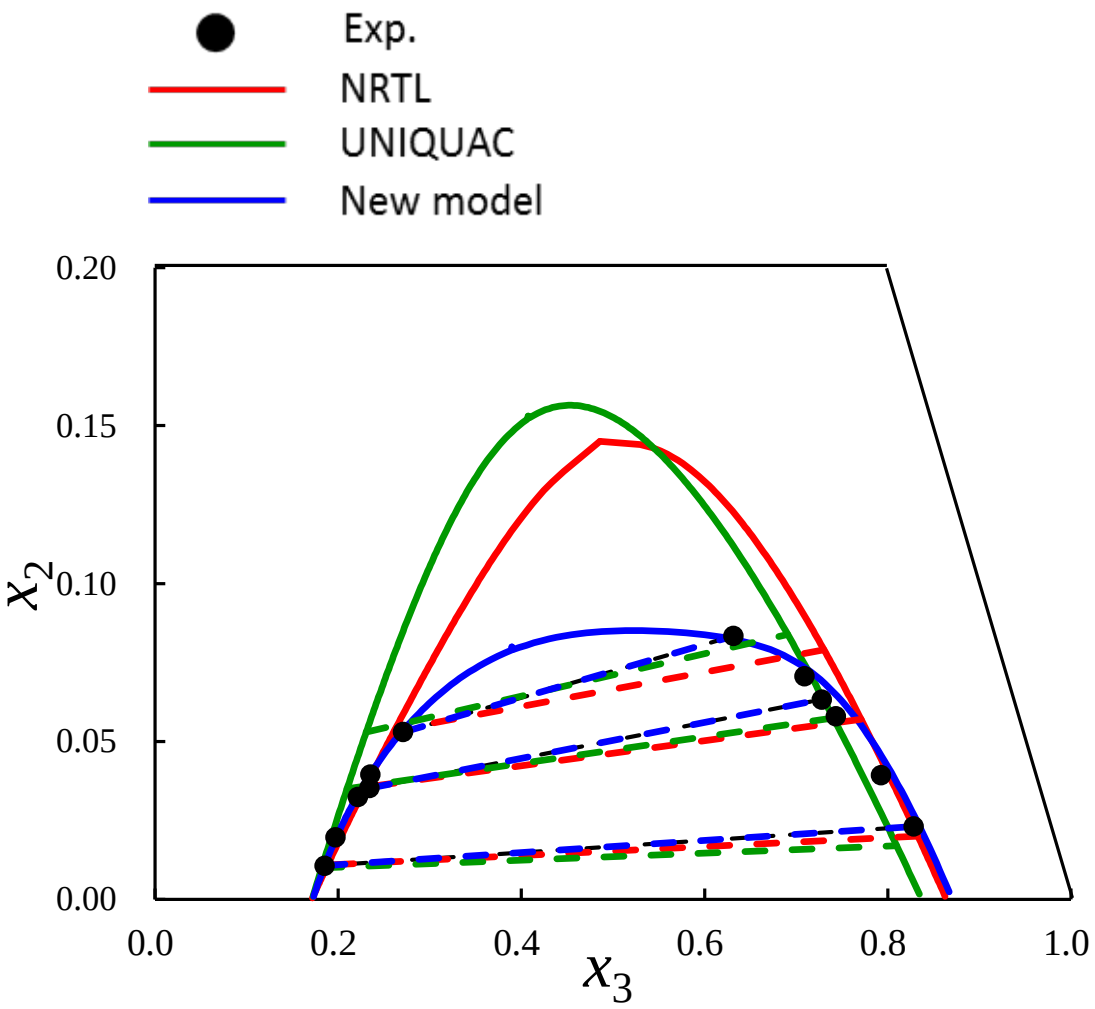
$q_1^0,\ q_2^0, q_3^0$

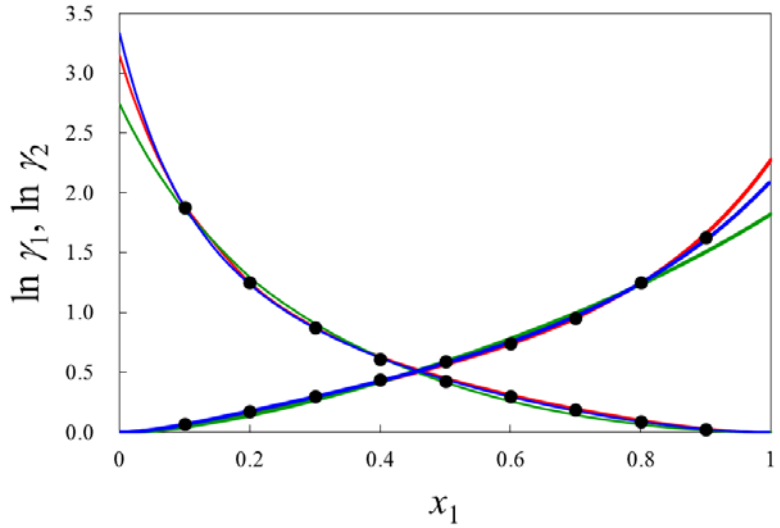
$q_{21}^\infty,\ q_{12}^\infty,\ q_{32}^\infty,\ q_{23}^\infty,\ q_{31}^\infty, q_{13}^\infty$

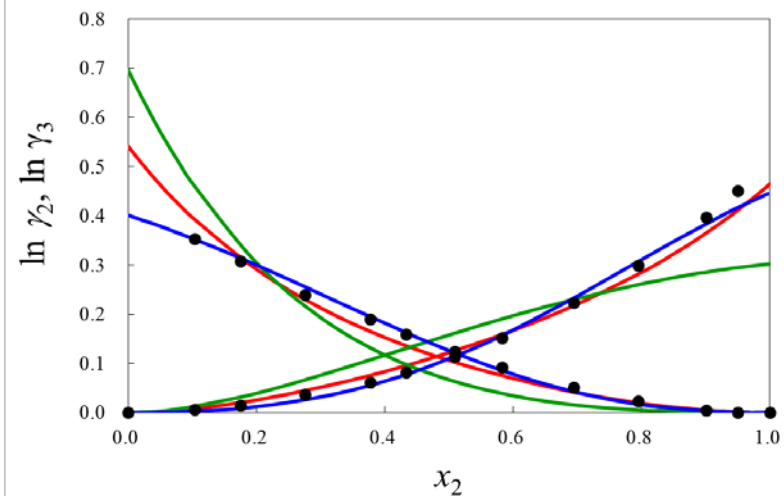
$\Delta E_{12}, \Delta E_{23},\ \Delta E_{13}$

Fix any one to any value

Methanol(1)+Benzene(2)+Cyclohexane(3) at 25ºC





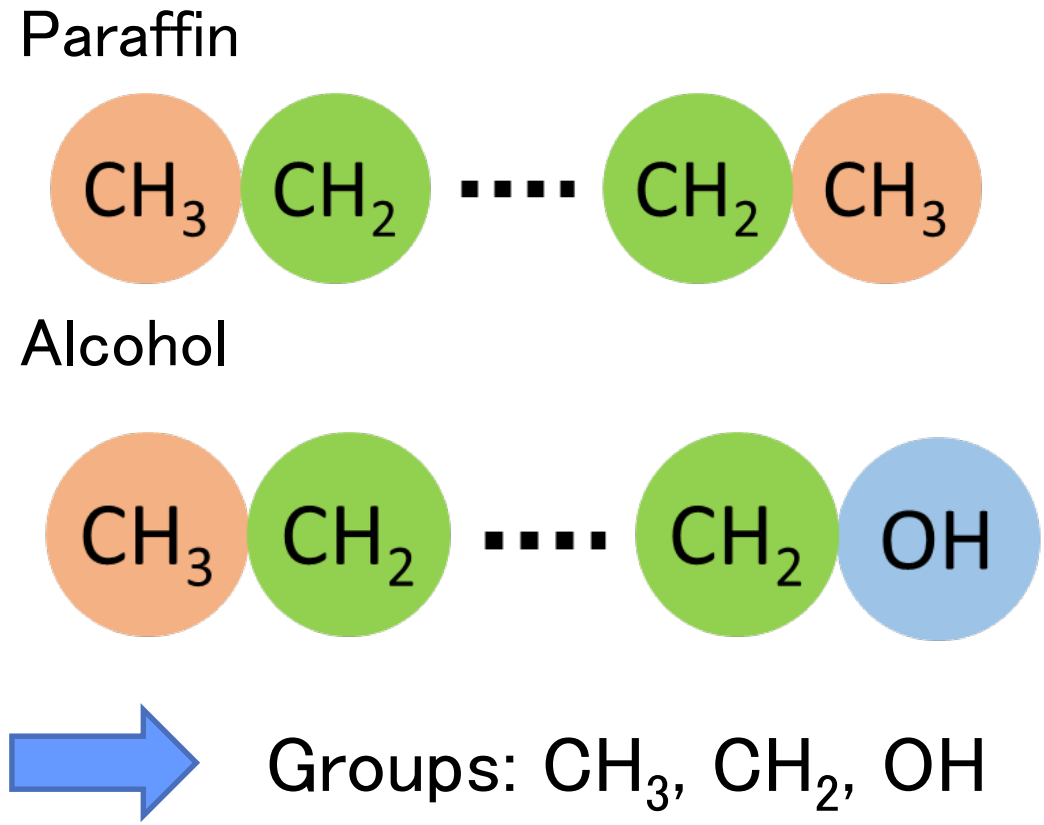


Exp. LLE: I. Nagata, Fluid Phase Equilib. 18 (1984) 83-92.
Exp.VLE (1)+(2): A. Iguchi, Kagaku Sochi 20 (1978) 66-68
Exp.VLE (2)+(3): A. Tasic, B. Djordjevic, D. Grozdanic, N. Afgan, D.Malic, Chem. Eng. Sci. 33 (1978) 189-197

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Group contribution method

A group contribution method uses the principle that group are always the same in many different molecules.



The properties of mixtures for paraffin and alcohol can be calculated by using the properties of groups CH_3, CH_2, and OH

ASOG [1)]

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^{G}$$

$$\ln \gamma_i^{FH} = \ln \frac{\nu_i^{FH}}{\sum_j \nu_j^{FH} x_j} + 1 - \frac{\nu_i^{FH}}{\sum_j \nu_j^{FH} x_j}$$

$$\ln \gamma_i^{G} = \sum_k \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right)$$

$$\ln \Gamma_k = - \ln \sum_{l=1}^{n} X_l a_{lk} + 1 - \sum_{l=1}^{n} \frac{X_l a_{lk}}{\sum_{m=1}^{n} X_m a_{lm}}$$

γ_i	: Activity coefficient of component *i*
γ_i^{FH}	: Contribution of molecular volume for activity coefficient of component *i* (Flory-Huggins contribution)
γ_i^{G}	: Contribution of interaction for activity coefficient of component *i*
ν_i^{FH}	: Number of atoms (other than hydrogen atoms) of component *i*
Γ_k	: Group activity coefficient of group *k* (Wilson equation)
$\Gamma_k^{(i)}$	: Group activity coefficient of group *k* in pure component *i*
ν_{ki}	: Number of atoms (other than hydrogen atoms) in group *k* of component *i*
x_i	: Mole fraction of component *i*
X_k	: Group mole fraction of group *k*
a	: Group interaction parameter

[1] T. Kojima, K. Tochigi, Prediction of vapor-liquid equilibria by ASOG, Kodansha (1976)

Extension to group contribution method

Basic model : ASOG[1)]

Modification from ASOG to present work

Flory–Huggins contribution ⇒ Ignore[2)]

Group interaction contribution: Wilson ⇒ New model

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{G}} = \sum_k v_{ki}\left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right) \quad , \quad X_k = \frac{\sum_i x_i v_{ki}}{\sum_i \sum_l x_i v_{li}}$$

γ_i	: Activity coefficient of component i
γ_i^{G}	: Contribution of interaction for activity coefficient of component i
Γ_k	: Group activity coefficient of group k
$\Gamma_k^{(i)}$	: Group activity coefficient of group k in pure component i
v_{ki}	: Number of atoms (other than hydrogen atoms) in group k of component i
x_i	: Mole fraction of component i
X_k	: Group mole fraction of group k

[1] T. Kojima, K. Tochigi, Prediction of vapor-liquid equilibria by ASOG, Kodansha (1976)
[2] K. Shinoda, J. H. Hildebr, J. Phys. Chem., 1961, 65, 1885–1886.

Group activity coefficient

$$\ln \Gamma_k = \sum_{l=k} \sum_{m>l} \left[-\Delta e_{lm} \left\{ Q_{l,k}\, \theta_m + \theta_l Q_{m,k} - (\theta_l \theta_m) \sum_n Q_{n,k} \right\} \right]$$

where,

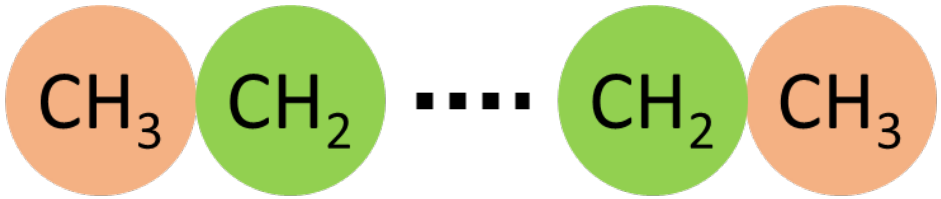
$$X_k = \frac{\sum_i x_i v_{ki}}{\sum_i \sum_l x_i v_{li}} \quad , \quad q_k = q_k^0 X_k + \sum_{l \neq k} q_{lk}^{\infty} X_l \quad , \quad \theta_k = \frac{(q_k X_k)}{\sum_l (q_l X_l)}$$

$$Q_{k,k} = q_k + X_k \left(q_k^0 - q_k \right) \quad , \quad Q_{l,k} = X_l (q_{kl}^{\infty} - q_l) \quad \text{where } l \neq k$$

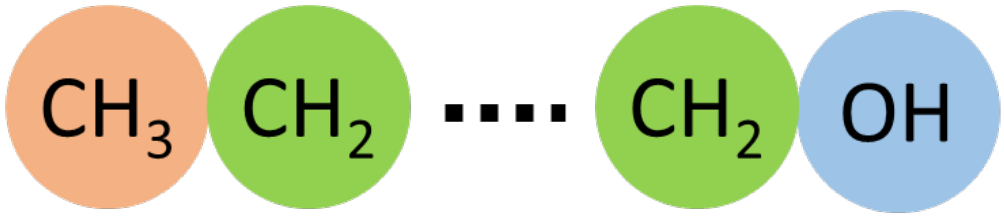
Δe_{kl}	: Exchange energy between groups k and l	x_i	:Mole fraction of component i
q_i^0	: q parameter of pure group i	X_k	:Group mole fraction of group k
q_{ji}^{∞}	: q parameter at infinite dilution	v_{ki}	:Number of atoms (other than hydrogen atoms) in group k of component i
θ_k	: Surface fraction of group k		

Groups

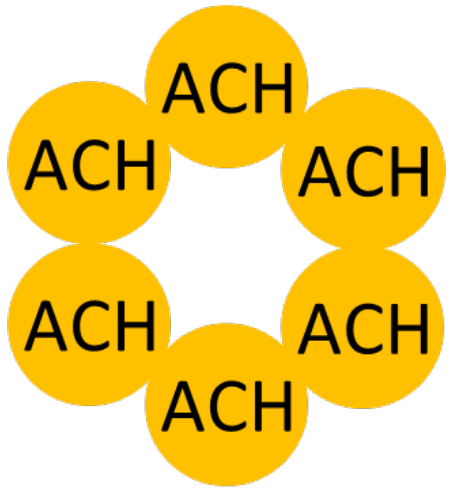
Paraffin



Alcohol



Benzene



Groups:CH_3, CH_2, OH, ACH

Experimental Data at 45±10℃ were used to determine parameter values.

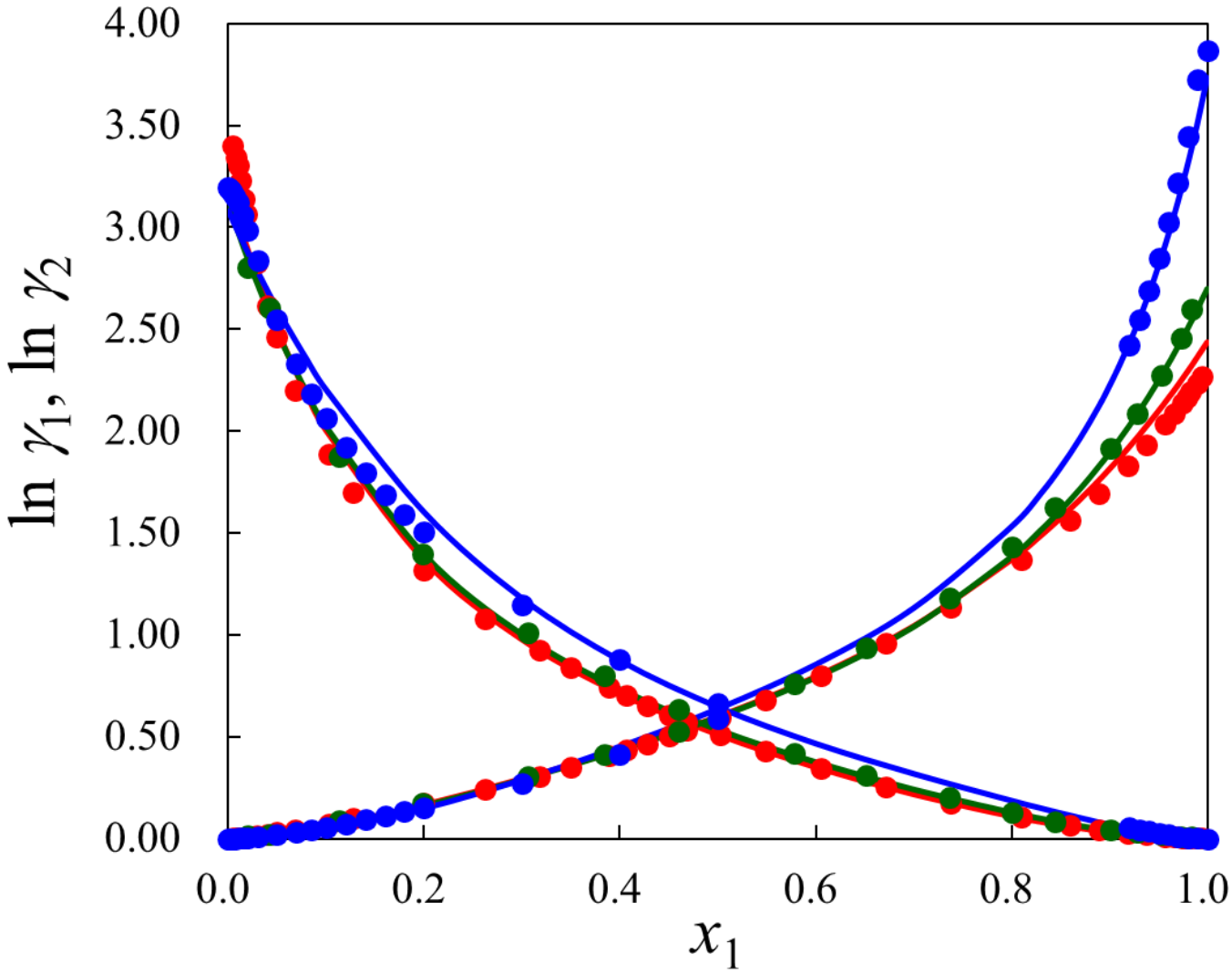
Parameter values for group contribution method

Fixed

q^0_{OH}	$q^0_{CH_3}$	$q^0_{CH_2}$	q^0_{ACH}
1.000	2.030	0.099	0.169

k	l	q^∞_{kl}	q^∞_{lk}	$-\Delta e_{kl}$
OH	CH_3	16.105	5.050	1.518
	CH_2	2.845	2.689	2.668
	ACH	1.737	1.294	4.370
CH_3	CH_2	0.791	0.614	0.000
	ACH	0.419	0.422	0.775
CH_2	ACH	0.032	0.589	0.000

Calculated results of ethanol(1)+paraffin(2) at 45 ˚C by new model

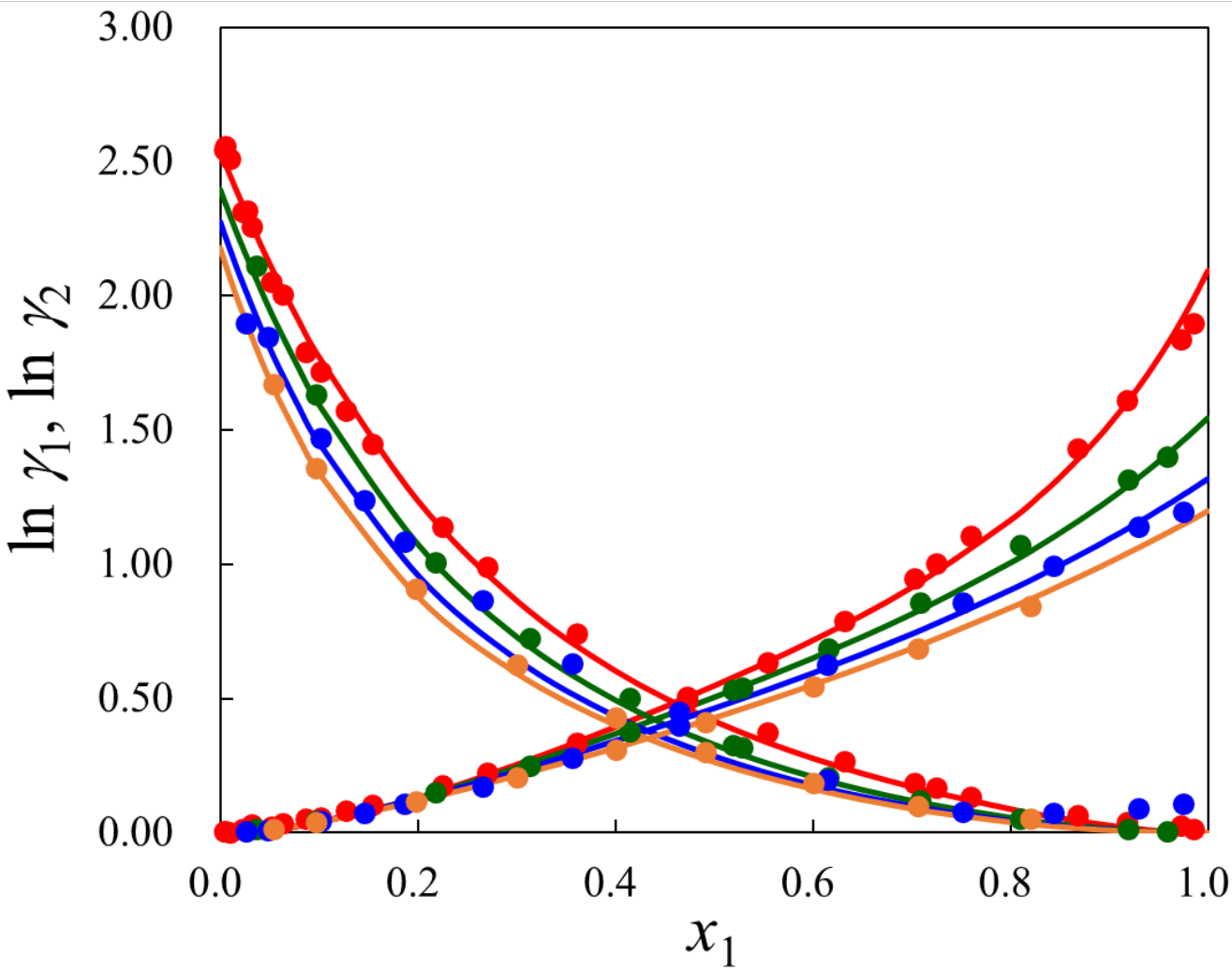


Since the data were used to determine the parameters of the new model, the comparisons were only as guide.

: ethanol(1)+hexane(2)[1]
: ethanol(1)+octane(2)[2]
: ethanol(1)+hexadecane(2)[3]
: ethanol(1)+hexane(2)
: ethanol(1)+octane(2)
: ethanol(1)+hexadecane(2)

[1] M. D. Pena, D. R. Cheda, An. Quim. 66, 721(1970)
[2] L. Boublikova, Lu B. C. -Y., J. Appl. Chem., 19, 89(1969)
[3] H. R. Stokes, et al., J. Chem. Thermodyn., 11, 671(1979)

Calculated results of alcohol(1)+benzene(2) at 45 ˚C by new model



Since the data were used to determine the parameters of the new model, the comparisons were only as guide.

: methanol(1)+benzene(2) [1]
: ethanol(1)+benzene(2) [2]
: 1-propanol(1)+benzene(2) [3]
: 1-butanol(1)+benzene(2) [4]

: methanol(1)+benzene(2)
: ethanol(1)+benzene(2)
: 1-propanol(1)+benzene(2)
: 1-butanol(1)+benzene(2)

Fig. Activity coefficients of alcohol(1)+benzene(2) for binary system at 45 ˚C.

[1] K. Strubl, V. Svoboda, R. Holub, Collect. Czech. Chem. Commun. 37, 3522(1972)
[2] Brown I., Smith F., Austr. J. Chem. 7, 264(1954)
[3] V. V. Udovenko, T. F. Mazanko, Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol. 15, 1654(1972)
[4] I. Brown, F. Smith, Austr. J. Chem. 12, 407(1959)

Conclusion

- I proposed a new model for activity coefficients.

  Y. Iwai, Fluid Phase Equilibria 465 (2018) 24-33*

  Y. Iwai, R. Seki, Y. Tanaka, Fluid Phase Equilibria 488 (2019) 62-71

  *** Fortran programs are downloadable for calculations of activity coefficients for binary and ternary systems)**

- Interaction number per molecule q depends on partner molecule and concentration
- The model is very flexible and accurate.
- The model can be applied to the systems which are very difficult to correlate.
- VLE and LLE can be correlate well with the same parameter set by the model.
- The model is extended to a group contribution method.